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CONDUCTIVITY, TEMPERATURE COEFFICIENTS OF CONDUCTIVITY, DISSOCIATION AND DISSOCIATION CONSTANTS OF CERTAIN ORGANIC ACIDS BETWEEN 0° AND 65°

By Leslie D. Smith and Harry C. Jones

[FOURTEENTH COMMUNICATION]

Historical

This investigation is a continuation of the work which has been in progress in this laboratory during the past twelve years on the conductivity, temperature coefficients of conductivity and dissociation of electrolytes between 0° and 65°. The work was undertaken in connection with the solvate theory of solution, which was proposed by Jones about thirteen years ago.

The first piece of work was done by Jones and West[1] on certain salts, and extended over the temperature range 0° to 35°.

The second investigation was by Jones and Jacobson[2] on a number of salts, over the same range in temperature.

The work of White and Jones[3] was on the conductivity, dissociation and dissociation constants of a number of organic acids from 0° to 35°.

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[1] This Journal, **34**, 357 (1905).

[2] *Ibid.*, **40**, 355 (1908).

[3] *Ibid.*, **42**, 520 (1909).

The fourth investigation was by Clover and Jones,[1] using organic acids and salts. The conductivities were measured from 35° to 80°. This was the first piece of work done in this laboratory over the higher range in temperature.

The second piece of work of White and Jones[2] was on the conductivity, dissociation and dissociation constants of a number of organic acids from 0° to 35°.

The second investigation of Jones and West[3] was on a number of salts between 35° and 65°.

The seventh investigation in this field was by Wightman and Jones,[4] on the conductivity, dissociation and dissociation constants of organic acids between 0° and 35°.

The eighth, by Hosford and Jones,[5] had to do with the conductivities, temperature coefficients of conductivity and dissociation of certain electrolytes from 0° to 35°.

The ninth, by Winston and Jones,[6] had to do with the conductivities, temperature coefficients of conductivity and dissociation of certain salts from 0° to 35°. Miss Winston worked out an interesting theory of induction in solution.

The second investigation by Wightman and Jones[7] had to do with the conductivity and dissociation of certain organic acids from 35° to 65°.

The eleventh investigation in this field was by Springer and Jones,[8] on the conductivity, dissociation and dissociation constants of a large number of organic acids between 0° and 65°.

The twelfth piece of work was done by Howard and Jones[9] on the conductivity, temperature coefficients of conductivity and dissociation of certain electrolytes between 35° and 65°.

The thirteenth research was carried out by Shaeffer and

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[1] This Journal, **43**, 187 (1910).

[2] *Ibid.*, **44**, 159 (1910).

[3] *Ibid.*, **44**, 508 (1910).

[4] *Ibid.*, **46**, 56 (1911).

[5] *Ibid.*, **46**, 240 (1911).

[6] *Ibid.*, **46**, 368 (1911).

[7] *Ibid.*, **48**, 320 (1912).

[8] *Ibid.*, **48**, 411 (1912).

[9] *Ibid.*, **48**, 501 (1912).

Jones[1] on the conductivity, temperature coefficients of conductivity and dissociation of certain salts; they also studied the effect of hydration and hydrolysis. In this investigation were studied a number of salts which had presented apparent abnormalities in the earlier work.

All of the above work, and that recorded in this paper which was done over the temperature range 35° to 65°, has been published as Monograph No. 170 by the Carnegie Institution of Washington.

The foregoing brief survey of the investigations in this laboratory is all that is necessary here, since the papers by White and Jones[2] and by Wightman and Jones,[3] already referred to, contain a careful review of the work previously done on the conductivity of organic acids in aqueous solution.

Purpose of this Investigation

The object in mind in carrying out this investigation was to secure more data concerning the dissociation of organic acids, over a wide range in temperature and dilution, to improve methods, to test the work already done in this laboratory, and to discover new relations between the additional data obtained.

Experimental

The investigation discussed in this paper has extended over about two years. The first year was devoted to a study of the conductivity and dissociation of certain organic acids at 35°, 50° and 65°. The acids used were some of those that had been studied at the lower temperatures by other workers in this laboratory. The readings at 35° were repeated, and the agreements were very satisfactory. Where the difference was appreciable the work was repeated. If the difference was still too great to be due to unavoidable experimental error, the readings at the lower temperatures were taken again and a complete set of data secured. The agreements were very close in practically every case, although the readings were taken by a different investigator. As has been stated, this work has already been published in Carnegie Institution of Washington Publication No. 170, which appeared in 1912.

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[1] This Journal, **49**, 207 (1913).

[2] *Ibid.*, **44**, 156 (1910).

[3] *Ibid.*, **46**, 56 (1911).

The work during this academic year has been devoted to the study of several acids at the lower temperatures, 0°, 12°.5, 25° and 35°.

The acids which had already been investigated by White and Jones at the lower temperatures and which were reinvestigated by the authors were: Hippuric, gallic, picric and crotonic. In every case very close agreements were found, and the values at 35° agreed to within the limits of experimental error. The temperatures were the same as those used by the former investigators.

Reagents

The water used in this work was purified in the same manner as that employed in the earlier series of investigations in this laboratory. This method was described in detail by Jones and Mackay.[1]

The acids used were obtained from Kahlbaum and Schuchardt. The general method of purification was recrystallization from conductivity water. The butyric acids—normal and iso—were purified by distillation in a vacuum; acetaminobenzoic acid was recrystallized from ether. Whenever possible the acids were carefully dried in a vacuum desiccator containing sulphuric acid. If practicable, the melting points of the acids were taken as one criterion of purity. The "mother" solution, *i. e.*, the one with the greatest concentration, was made up, whenever possible, by direct weighing, and then titrated against standard alkali. The acids which are liquids were made up directly by titration. The modification of this method for the higher temperatures was described in detail in the paper by Wightman and Jones.[2] All flasks and burettes used in this investigation were calibrated by the method of Morse and Blalock[3] and also by weight of the contained water.

The sodium salts of the organic acids were used to determine the μ_∞ values of the acids, and were prepared by titration. It was found by previous work that the sodium salts of organic acids, in general, are completely dissociated at a dilution of $V = 2048$. Therefore, a solution of the acid at this dilution was just neutralized by sodium hydroxide, using phenolphthalein as the indicator, and its conductivity was determined in the usual way.

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[1] This Journal, **19**, 91 (1897).

[2] *Ibid.*, **48**, 320 (1912).

[3] *Ibid.*, **16**, 479 (1894).

Apparatus

The cells used in this investigation were the same as those employed by Jones and Wightman. In their paper they state:[1]

"The cells resembled those used by Jones and Bingham,[2] with platinum-plate electrodes, attached to glass tubes containing mercury, the tubes being sealed into ground glass stoppers. As many as eight cells were employed with constants ranging from about 10 to 330 in Siemens' units. A cell of special type,[3] having a very low constant, was used for obtaining the conductivity of the water.

"In order to get a sharp reading in the cells, the electrodes were covered with a fine coating of platinum black, in the usual manner."

The thermometers used were carefully calibrated against a standard Reichsanstalt thermometer. The standard thermometer was also calibrated at the United States Bureau of Standards.

The resistance box which was used throughout this entire investigation had also been calibrated by the Bureau of Standards. A very fine slide wire bridge was employed, the wire being wrapped around a marble drum. On this bridge the investigator could easily read to fractions of a millimeter. The entire scale was five meters long and readings could be made to tenths of a millimeter.

The cells were kept at constant temperature in thermostats. As this work was carried on simultaneously with that of Dr. Wightman, and partly using his apparatus, reference is made to his description of the system of thermal regulation. In the papers by Wightman and Jones[1] the system of regulation for temperatures, 0° to 35°, is fully described. They say:

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[1] THIS JOURNAL, **46**, 62 (1911).

[2] *Ibid.*, **34**, 493 (1905).

[3] *Ibid.*, **45**, 282 (1911).

"Three thermostats were employed to keep the cells at constant temperature; one for 0° similar to that described by Jones and Jacobson;[2] one for 15° (in this case for 12°.5) and 25°, a galvanized tub containing 20 to 30 liters of water, and in the bottom of which was placed a lead (in this investigation, copper) coil through which cold water was passed under constant pressure; a third for 35°, differing from the latter only in not having a coil in the bottom. They were both kept constantly stirred by propellers driven by a hot air engine. In this way it was possible to keep the temperature constant to within 0°.02."

The work at the more elevated temperatures was carried out in apparatus similar to that used at the lower temperature, with the difference that the thermostats were covered with asbestos boards saturated with paraffin. The thermometer and stirrer passed through small openings in the cover, and the cells were placed in the bath through openings just large enough to admit them. These holes were covered by pieces of the same material as the cover. The evaporation of the water in the bath was in this way reduced to a minimum, and the confined vapors maintained the cells, both the exposed portion and the part immersed in the bath, at the same temperature.

Thermoregulators of the same type as are used throughout this laboratory were employed. They need not be described here since this has so often been done in THIS JOURNAL.

There has been much less work done here at higher than at lower temperatures, therefore a more detailed description of the various difficulties encountered, and the methods devised to overcome them, will be given.

The only work that had been previously carried out here is that of Clover and Jones[3] and West and Jones.[4]

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[1] THIS JOURNAL, **46**, 56 (1911).

[2] *Ibid.*, **40**, 355 (1908).

[3] *Ibid.*, **43**, 187 (1910).

[4] *Ibid.*, **44**, 508 (1911).

This investigation was carried on simultaneously with those of Jones and Wightman[1] and of Springer and Jones,[2] and partly with the same apparatus used by Jones and Springer; and Dr. Springer and the authors worked out together the various problems in connection with the measurements at higher temperatures.

Procedure

The cell constants were taken by the method described by White and Jones.[3] When working at low temperatures they were determined as often as once a month, and still more frequently when working at high temperatures.

The experimental difficulties are much more numerous at the higher than at the lower temperatures. There is a greater and more frequent variation in the cell constants. The solubility of the glass is often too large to be negligible. A few short quotations from the work of Clover and Jones, referred to above, will give the results of their investigations in the best possible form.

Cell Constants.—"It has developed that a strain is brought about by the high temperatures, which may result in a change either in the distance of the electrode plates from each other or in the surface of the plates.

"Since such a variation had not previously been observed in work covering a range of 0° to 35°, it was thought that the changes might be reduced by maintaining the cells at a temperature which was about a mean of those employed in the experimental work. Accordingly, when not in use, the cells were filled with pure water and placed in a bath which was maintained continuously at a temperature of 45° to 50°."

They performed an experiment to test the value of this method.

"The measurements were first carefully made at 35° and then duplicated; then the regular systematic procedure was gone through at 65°, and after this the readings at 35° were again made. If the results obtained the second time should agree with those first obtained at 35°, this would be strong evidence that the method was reliable. It was found in some cases that the second reading differed slightly from the first. In other cases there was no difference, and the change appeared to be independent of the cell used, or the concentration of the solution. It was found, further, that on standing for a considerable length of time at 35° (2 or 3 hours), *the reading slowly changed back in all cases to the original value.* It is difficult to see what other causes can be assigned to these results than a temporary change in the cell constant during the heating at 65°."

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[1] This Journal, **48**, 320 (1912).

[2] *Ibid.*, **48**, 411 (1912).

[3] *Ibid.*, **42**, 520 (1909).

In conductivity work carried out at the ordinary temperatures, experiments have shown that the error introduced by the solubility of the glass is negligible. However, at 50° the error from this same source at a dilution of one liter is the largest of all the ordinary experimental errors. The glass is still more soluble at 65°, as would be expected. Clover and Jones point out that at 80° the conductivity of pure water is increased tenfold on standing in the cells for a couple of hours. The cells used in their research were made of hard glass. Obviously, the amount of glass dissolved from the cells depends largely upon the nature of the glass of which the cells are made. It varies considerably with the different cells. As a result of this we abandoned the attempt of introducing directly a correction factor for the solubility of glass. This source of error was overcome in another way.

It was found that after the cells had been heated with water for several hours the amount of glass dissolved gradually decreased and finally became practically nothing. After this treatment, as the cells were kept in a bath at 45° and 65° and the water in them changed once a day, the solubility of the glass at 65° was always practically zero and therefore negligible. If a cell was removed from the bath and allowed to stand filled with water at room temperature for any appreciable length of time, it was found on heating that glass was again dissolved.

In this investigation the above named precautions were all observed. In addition, at the start of the work the glass vessels were heated with a dilute solution of caustic soda, then boiled with dilute hydrochloric acid and then for some time with conductivity water. The solubility of the glass was shown by tests to have been reduced to a negligible quantity by this treatment. The cells were then kept filled with conductivity water, which was changed every day, and were maintained at a temperature which was approximately 50°, and thus the solubility of the glass was negligible. This was proved experimentally. A cell was filled with conductivity water at 35° and the conductivity read; then it was heated and readings were made at both 50° and 65°. The solution was cooled to 35° and the conductivity again measured. Since the two readings at 35° coincided, there was no appreciable quantity of glass dissolved during the process.

This was not the only beneficial result obtained from keeping the cells always at an elevated temperature. The expansion of glass and of platinum is not large enough to affect appreciably the cell constants, as would be the case if the temperature varied over a wider range.

It has already been stated that it takes several hours for a cell to acquire its normal condition at the lower temperature with respect to the electrode-plates and the glass rods when suddenly cooled. This fact was utilized in the determination of the cell constants at the higher temperatures. The cells were kept at about 50° and when the cell constants were to be taken, the cells were filled with the solution of potassium chloride and they were heated to 50° for about one hour. The cells containing the solution were then cooled down and the conductivity read immediately after a constant temperature had been reached. The readings were made at 25°, where the conductivity of the solutions of potassium chloride is accurately known.

The method of White and Jones was used for taking the cell constants over the entire range of temperature from 0° to 65°.

Two objects were accomplished in all the work at higher temperatures by filling the cells nearly to the top with the solutions. First, evaporation and the consequent change in concentration were reduced to a minimum. Second, carbon dioxide and other gases from the air were prevented from being present in sufficient quantity to affect the results.

The method of preparing the solutions was that devised by West and Jones:

"Since we worked over a range of temperature of only 30°, we found it convenient to prepare the solutions at the intermediate temperature, 50°, and then to use the solutions at the three temperatures, 35°, 50° and 65°. But since the volume of a solution varies with the temperature it was, of course, necessary to apply a correction at 35° and 65° to the volume of solutions made up to 50°.

"When a standard solution is cooled from 50° to 35° there is a contraction in volume and a subsequent increase in the concentration of the solution. The value of μ_v for any solution would, therefore, be slightly too large. The value of μ_v as found must be multiplied by the factor 0.994 for results at 35° when the solutions were made up at 50°. The correction factor for solutions made up at 50° and used at 65° is 1.0076.

"The coefficient of expansion for distilled water is somewhat less than that for an aqueous solution. However, the difference in the coefficients for water and for that of our most concentrated solution is so small that it is negligible.

"By making use of the above correction it was necessary to prepare only one set of solutions for each salt; and, consequently, much pure material and time were saved."

When Wightman, Springer and the authors began the investigations at the higher temperatures the two problems presenting themselves were:

First.—In making up the solutions at 50° the glass of the flasks would dissolve, because the flasks were not kept at 50° in a bath, but, when not in use, were allowed to cool down to room temperature.

Second.—The solution, even if heated to 50°, would cool off when poured into the burette, and still further when being drained into the flask; therefore, instead of drawing off 50 cc.

of the solution at 50°, there would be drawn off 50 cc. at a temperature of 50° − x°, or more than 50 cc. at 50°.

This complex source of error was overcome by the above named workers, all of whom started simultaneously the present line of work at elevated temperatures. The results are given in the paper by Springer and Jones.[1]

"A simple device did away with both of these sources of error. At 50°, 988.07 grams of distilled water have a volume of 1000 cc. Our liter flask was weighed at 20°. Then 988.07 grams of distilled water at 20° were introduced—air displacement being taken into account. The flask was marked at the bottom of the meniscus. This flask, filled to the mark with water at 20° (room temperature), will contain a liter at 50°. Therefore, all the mother solutions could be made up for 50° work at 20°, and the solubility of the glass, which is noticeable only at higher temperatures, is thus made negligible.

"This mother solution will be, let us say, normal at 50°. At 20° it is stronger than normal. If we draw out 100 cc. at 20° and dilute it to 200 cc. at 20°, it will also be stronger than half-normal. But heat this latter solution to 50° and it will again attain its required normality—assuming that the coefficient of expansion of water is the same as that of dilute solutions. And all solutions worked with were eighth-normal, or more dilute. This permits us to titrate all solutions at room temperature, which obviates the second of the above difficulties."

This solution of the above-mentioned problems was worked out by Springer and Jones and the authors jointly, and with the same apparatus. We used a 500 cc. or a 200 cc. flask calibrated in this way for 50° at 20°, in which to make up our mother solutions.

In the higher temperature work it was noted that bubbles of air formed on the electrodes, especially at 50° and 60°. These were removed by shaking the cells thoroughly before making the readings.

Values

The values of the limiting conductivities of the monobasic acids were found directly from the μ_∞ values of their sodium salts. It has been shown by experiment that the conductivities of sodium salts, made up by the titration method, which, as we have already stated, was used in this work, agree with the conductivities of solutions which were made up directly from the dry, solid sodium salt. The μ_∞ values of the acids were obtained from those of the sodium salts by a very simple method. It consists in subtracting the constant of the sodium ion from the limiting conductivity value of the sodium salt, and then adding to this value the constant of the hydrogen ion. This may be readily accomplished in actual work by using this equation: μ_∞ acid = μ_∞ HCl + μ_∞ Na salt of acid — μ_∞ NaCl.

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[1] THIS JOURNAL, **48**, 417 (1912).

To calculate the value of μ_∞ for hydrochloric acid and sodium chloride at the various temperatures at which the work was done, we used the equations of White and Jones.

For sodium chloride,

$$\mu_\infty = 63.04 + 2.04\,t - 0.00823\,t^2$$

For hydrochloric acid,

$$\mu_\infty = 245.4 + 6.06\,t - 0.00776\,t^2$$

In the table on page 14 are given all the values of the acids with which we worked. The μ_∞ values of the dibasic acids could not be determined by this method. The sodium salts of dibasic acids do not yield a maximum value of conductivity at dilutions at which work could be done. Comparison of the μ_∞ values of the acids which Jones and several of his coworkers have studied shows that those acids with the largest number of atoms in the anions have the smallest μ_∞ values.

A curve, in which the ordinates represent the μ_∞ values of the acids, and abscissas, the number of the atoms, was plotted for all the acids studied in this field by Jones and his coworkers.[1] By placing the dibasic acids on this curve according to the number of atoms present, their values were obtained. (See Fig. 1.)

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[1] Carnegie Institution of Washington, Publication No. **170**.

The values of the acids marked * in the table were determined by other workers in this laboratory, and can be found in Publication of the Carnegie Institution of Washington, No. 170, pp. 91–92. It was shown that acids having the same number of atoms in the molecule have the same μ_∞ value. From these values and the others given in the table just referred to the curve was, therefore, plotted. On this curve it was possible

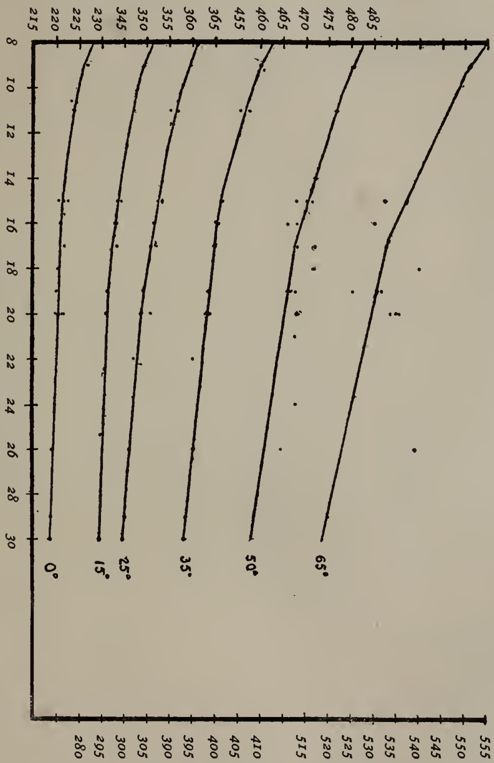

Fig. I.—Limiting Conductivities.

to find the values of μ_∞ for the dibasic acid by means of the graphic method previously described. It can be seen by glancing at the curve that at the higher temperatures the method is far less accurate, since the values which are determined directly, using the sodium salt, fall less frequently on a definite curve at the higher temperatures.

Limiting Conductivities of the Acids

	0°	12°.5	25°	35°	50°	65°
Butyric*	...	...	...	404	473.3	540.3
Isobutyric*	...	...	...	403	437.29	468.7
Malic	221.5	286.2	352	400	...	...
Pyrotartaric*	...	...	...	397	468	533
Racemic*	...	...	...	398	468.2	534.9
Hippuric	219	280	345	392	446.4	499.8
Citric*	...	...	...	392	464.5	528.5
Aconitic	220.2	285	350	398	...	...
Crotonic	222	286	352	402	475.1	544
Maleic*	...	...	...	402	475	544
Fumaric*	...	...	...	402	475	544
Itaconic*	...	...	...	400	471	537.5
Citraconic*	...	...	...	400	471	537.5
Mesaconic*	...	...	...	400	471	537.5
m-Chlorobenzoic	222.4	285.3	350.5	398.5	...	...
p-Chlorobenzoic	222	285.2	353.5	400	...	...
o-Bromobenzoic	223	286.5	352.5	401	...	...
m-Bromobenzoic	222.8	285	352.6	401.6	...	...
m-Hydroxybenzoic	219.7	285.8	350.8	397.3	...	...
m-Acetoxybenzoic	220.4	284	349.1	397	...	...
o-Sulphobenzoic	220	284.5	349.5	397.5	...	...
m-Sulphobenzoic	220	284.5	349.5	397.5	...	...
Picric	207	281.6	331	380	451.6	506.8
Gallic	220	...	348	396	459.1	514.3
Aminobenzenesulphonic	221	285	350	398	...	...
o-Toluic*	...	...	...	397	470.1	536
m-Toluic*	...	...	...	397	470.4	541.9
p-Toluic*	...	...	...	397	469.1	538.8
Mandelic	...	...	...	397	475.4	539.9
Sebacic	218	284	343.5	391	...	...

The results of our conductivity measurements are tabulated in the following pages. The molecular conductivities (μ_v) are expressed in Siemens' units.

Temperature coefficients are expressed in both conductivity units and percentages. The former are obtained by the equation

$$(\mu_{t_1} - \mu_t) / (t_1 - t) = \textit{conductivity units}$$

the latter by the equation

$$(\mu_{t_1} - \mu_t) / \mu_{t_1}(t_1 - t) = \textit{per cent. temperature coefficient}^{[1]}$$

where t = the lower temperature, t_1 the next higher temperature, μ_t and μ_{t_1} the conductivities of the same solution measured at temperatures t and t_1, respectively.

Obviously the percentage dissociation may be expressed as

$$\alpha = \mu_v / \mu_\infty$$

The dissociation constants are obtained from Ostwald's dilution law

$$\alpha^2 / (1 - \alpha) V = K$$

This is found to hold for the weaker organic acids. In the tables where no values are given for $K \times 10^4$, the acids were so strong that they did not obey the law.

Butyric Acid, $CH_3CH_2CH_2COOH$

Molecular Conductivity

V	45°	50°	65°
2	1.93	2.22	2.41
8	4.35	4.86	5.26
32	8.80	9.95	10.80
128	17.14	19.77	21.23
512	33.00	37.80	41.11
1024	...	...	...
2048	62.71	70.83	77.48

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
2	0.019	0.98	0.013	0.59
8	0.034	0.78	0.027	0.55
32	0.077	0.87	0.057	0.57
128	0.176	1.03	0.097	0.49
512	0.32	0.97	0.221	0.58
1024	...	....	...	....
2048	0.54	0.86	0.443	0.62

Limiting Conductivity

35° 404 50° 473.3 65° 540.3

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[1] Z. physik. Chem., **2**, 561 (1888).

Percentage Dissociation

V	35°	50°	65°
2	0.48	0.47	0.45
8	1.08	1.03	0.97
32	2.18	2.10	2.00
128	4.24	4.18	3.93
512	8.17	7.98	7.61
1024	...	...	...
2048	15.52	14.96	14.34

Dissociation Constants

V	35°	50°	65°
2	0.115	0.111	0.102
8	0.147	0.133	0.118
32	0.152	0.141	0.127
128	0.147	0.142	0.125
512	0.142	0.135	0.122
1024	...	...	...
2048	0.139	0.128	0.117

Isobutyric Acid, $CH(CH_3)_2COOH$

Molecular Conductivity

V	35°	50°	65°
2	1.74	1.97	2.11
8	3.96	4.41	4.76
32	7.88	8.83	9.44
128	15.60	17.60	18.60
512	30.35	33.71	35.81
1024	41.53	46.27	49.01
2048	56.35	60.92	64.01

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
2	0.015	0.88	0.009	0.47
8	0.030	0.75	0.024	0.54
32	0.063	0.80	0.041	0.46
128	0.133	0.85	0.067	0.38
512	0.224	0.73	0.14	0.41
1024	0.316	0.76	0.18	0.39
2048	0.305	0.54	0.21	0.34

Limiting Conductivity

35°	403	50°	437.29	65°	468.7

Percentage Dissociation

V	35°	50°	65°
2	0.43	0.45	0.45
8	0.98	1.01	1.02
32	1.96	2.02	2.01
128	3.87	4.02	3.97
512	7.53	7.71	7.64
1024	10.30	10.58	10.46
2048	13.98	13.93	13.66

Dissociation Constants

V	35°	50°	65°
2	0.093	0.102	0.102
8	0.121	0.128	0.131
32	0.121	0.130	0.129
128	0.122	0.131	0.128
512	0.119	0.125	0.123
1024	0.115	0.122	0.119
2048	0.110	0.110	0.123

Malic Acid, $HOOCCH_2CH(OH)COOH$

Molecular Conductivity

V	0°	12°.5	25°	35°
32	26.84	35.97	44.45	51.18
128	46.73	62.83	78.46	90.47
512	79.42	106.41	132.70	152.89
1024	103.59	138.48	172.50	198.11
2048	128.27	170.97	211.16	243.84

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
32	0.73	2.71	0.67	1.86	0.67	1.50
128	1.28	2.73	1.25	1.98	1.20	1.52
512	2.16	2.71	2.10	1.97	2.01	1.51
1024	2.79	2.69	2.72	1.96	2.56	1.48
2048	3.41	2.65	3.21	1.87	3.26	1.53

Limiting Conductivity

0° 221.5 12°.5 286.2 25° 352 35° 400

Percentage Dissociation

V	0°	12°.5	25°	35°
32	12.11	12.56	12.62	12.79
128	21.05	21.95	22.28	22.61
512	35.85	37.18	37.69	38.22
1024	46.76	48.38	49.00	49.52
2048	57.90	59.73	59.98	60.96

Dissociation Constants

V	0°	12°.5	25°	35°
32	5.21	5.63	5.69	5.86
128	4.38	4.82	4.98	5.16
512	3.91	4.29	4.45	4.61
1024	4.03	4.42	4.59	4.74
2048	3.88	4.22	4.38	4.64

Pyrotartaric Acid, $CH_3CH(COOH)CH_2COOH$

Molecular Conductivity

V	35°	50°	65°
8	10.39	12.10	13.77
32	20.95	24.36	27.28
128	40.05	46.80	52.92
512	75.04	86.64	98.14
1024	....	....	....
2048	135.89	157.90	176.35

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	0.12	1.03	0.11	0.82
32	0.22	1.05	0.29	0.79
128	0.43	1.07	0.38	0.82
512	0.77	1.03	0.76	0.88
1024	....	....	....	....
2048	1.46	1.07	1.23	0.77

Limiting Conductivity

35° 397 50° 468 65° 533

Percentage Dissociation

V	35°	50°	65°
8	2.62	2.58	2.58
32	5.28	5.20	5.11
128	10.08	10.00	9.92
512	18.90	18.51	18.41
1024	....	...	...
2048	34.22	33.73	33.08

Dissociation Constants

V	35°	50°	65°
8	0.88	0.85	0.85
32	0.91	0.89	0.85
128	0.88	0.86	0.85
512	0.86	0.82	0.81
2048	0.86	0.83	0.79

Racemic Acid, $(C_4H_6O_6)_2.2H_2O$

Molecular Conductivity

V	35°	50°	65°
8	34.79	39.97	44.88
32	68.02	77.91	87.21
128	123.8	141.44	158.41
512	214.9	243.91	271.34
1024	263.1	302.97	336.09
2048	332.6	375.37	414.73

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	0.34	0.99	0.33	0.82
32	0.66	0.97	0.62	0.80
128	1.17	0.95	1.13	0.80
512	1.93	0.90	1.83	0.75
1024	2.59	0.97	2.21	0.73
2048	2.85	0.86	2.62	0.70

Limiting Conductivity

35° 398   50° 468.2   65° 534.9

Percentage Dissociation

V	35°	50°	65°
8	8.75	8.53	8.39
32	17.08	16.64	16.30
128	31.09	30.21	29.61
512	53.98	52.09	50.72
1024	66.09	64.7	62.83
2048	83.55	80.2	77.53

Dissociation Constants

V	35°	50°	65°
8	10.43	9.94	9.60
32	10.99	9.96	9.91
128	12.19	10.36	9.63
512	12.36	11.06	10.19
1024	12.57	10.92	10.37
2048	20.72	14.80	13.06

Hippuric Acid, $C_6H_5CONHCH_2COOH$

Molecular Conductivity

V	0°	12°	25°	35°	50°	65°
128	33.86	43.92	55.16	61.58	70.76	77.97
512	61.60	79.81	100.01	113.98	131.23	184.77
1024	80.81	104.72	130.90	147.23	169.15	186.18
2048	102.70	133.96	165.70	187.00	219.90	242.15

Temperature Coefficients (Cond. Units)

V	0°–12°	12°–25°	25°–35°	35°–50°	50°–65°
128	0.84	0.086	0.64	0.61	0.48
512	1.52	1.55	1.40	1.15	0.90
1024	1.99	2.00	1.63	1.46	1.13
2048	2.60	2.44	2.13	2.20	1.48

Temperature Coefficients (Per Cent.)

V	0°–12°	12°–25°	25°–35°	35°–50°	50°–65°
128	2.48	1.95	1.16	0.99	0.67
512	2.46	1.94	1.39	1.00	0.68
1024	2.46	1.99	1.24	0.99	0.66
2048	2.53	1.82	1.28	1.10	0.68

Limiting Conductivity

0° 219   12° 280   25° 345   35° 392   50° 446.4   65° 499.8

Percentage Dissociation

V	0°	12°	25°	35°	50°	65°
128	15.46	15.68	15.98	15.70	15.85	15.60
512	28.12	28.50	28.98	29.07	29.38	28.97
1024	36.89	37.39	37.94	37.55	37.87	37.25
2048	46.89	47.84	48.02	47.70	49.24	48.45

Dissociation Constants

V	0°	12°	25°	35°	50°	65°
128	2.21	2.27	2.37	2.28	2.33	2.25
512	2.14	2.22	2.30	2.32	2.38	2.30
1024	2.10	2.18	2.26	2.20	2.25	2.16
2048	2.02	2.14	2.16	2.12	2.33	2.23

Citric Acid, $HOOCC(OH)(CH_2COOH)_2.H_2O$

Molecular Conductivity

V	35°	50°	65°
8	31.85	37.91	43.77
32	63.49	75.80	86.99
128	114.41	136.44	155.61
512	197.41	234.37	267.22
1024	252.94	305.21	338.70
2048	301.63	357.77	410.66

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	0.41	1.27	0.39	1.02
32	0.82	1.29	0.75	0.98
128	1.47	1.28	1.28	0.93
512	2.46	1.29	3.28	0.93
1024	2.93	1.25	4.35	0.95
2048	3.74	1.24	5.29	0.98

Limiting Conductivity

35° 392   50° 464.5   65° 528.5

Percentage Dissociation

V	35°	50°	65°
8	8.12	8.16	8.28
32	16.19	16.31	16.46
128	29.18	29.37	29.44
512	50.35	50.45	50.56
1024	64.52	65.70	64.08
2048	76.94	77.02	77.70

Dissociation Constants

V	35°	50°	65°
8	8.97	9.06	9.34
32	9.77	9.93	10.13
128	9.38	9.55	9.59
512	9.97	10.36	10.09
1024	11.45	12.28	11.16
2048	12.53	12.60	13.21

Aconitic Acid, $HOOCCH{:}C(COOH)CH_2COOH$

Molecular Conductivity

V	0°	12°.5	25°	35°
32	24.80	33.13	41.29	47.21
128	41.91	55.75	69.28	79.67
512	64.71	85.51	105.67	121.09
1024	79.12	104.19	128.78	146.92
2048	91.19	120.09	149.67	169.80

Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
32	0.67	2.68	0.65	1.96	0.59	1.43
128	1.11	2.63	1.08	1.94	1.01	1.45
512	1.66	2.56	1.61	1.88	1.54	1.45
1024	2.00	2.53	1.97	1.88	1.81	1.40
2048	2.31	2.53	2.37	1.97	2.01	1.34

Limiting Conductivity

0°	12°.5	25°	35°
220.2	285	350	398

Percentage Dissociation

V	0°	12°.5	25°	35°
32	11.26	11.61	11.80	11.86
128	19.03	19.54	19.79	19.94
512	29.38	29.98	30.19	30.42
1024	35.93	36.53	36.79	36.91
2048	41.41	42.10	42.76	42.66

Dissociation Constants

V	0°	12°.5	25°	35°
32	4.46	4.76	4.93	4.98
128	3.49	3.70	3.81	3.87
512	2.38	2.50	2.54	2.59
1024	1.96	2.05	2.09	2.10
2048	1.42	1.49	1.55	1.54

Crotonic Acid, $CH_3CH{:}CHCOOH$

Molecular Conductivity

V	0°	12°	25°	35°	50°	65°
8	2.73	3.62	4.52	5.16	5.92	6.56
32	5.49	7.27	9.09	10.30	11.90	13.13
128	10.90	14.42	17.92	20.27	23.88	26.20
512	21.23	28.20	35.14	39.83	46.54	57.73
1024	29.09	38.50	48.04	54.60	62.67	69.54
2048	39.68	53.41	65.33	74.15	88.44	98.12

Temperature Coefficients (Cond. Units)

V	0°–12°	12°–25°	25°–35°	35°–50°	50°–65°
8	0.07	0.07	0.06	0.05	0.04
32	0.15	0.14	0.12	0.11	0.08
128	0.29	0.27	0.23	0.24	0.15
512	0.58	0.53	0.47	0.45	0.35
1024	0.78	0.73	0.66	0.54	0.46
2048	1.14	0.99	0.88	0.95	0.64

Temperature Coefficients (Per Cent.)

V	0°–12°	12°–25°	25°–35°	35°–50°	50°–65°
8	2.69	1.92	1.38	0.97	0.72
32	2.69	1.91	1.31	1.07	0.68
128	2.72	1.86	1.27	1.18	0.64
512	2.74	1.89	1.34	1.13	0.74
1024	2.68	1.91	1.37	0.99	0.73
2048	2.67	1.90	1.35	1.28	0.72

Limiting Conductivity

0°	12°	25°	35°	50°	65°
222	286	352	402	475.1	544

Percentage Dissociation

V	0°	12°	25°	35°	50°	65°
8	1.22	1.26	1.28	1.28	1.24	1.21
32	2.47	2.54	2.58	2.56	2.50	2.41
128	4.90	5.04	5.08	5.04	5.02	4.82
512	9.56	9.86	9.97	9.90	9.79	9.51
1024	13.10	13.46	13.64	13.58	13.19	12.78
2048	17.87	18.67	18.55	18.44	18.60	18.03

Dissociation Constants

V	0°	12°	25°	35°	50°	65°
8	0.188	0.200	0.207	0.207	0.195	0.185
32	0.195	0.206	0.213	0.210	0.200	0.185
128	0.197	0.208	0.212	0.208	0.209	0.190
512	0.197	0.210	0.215	0.212	0.205	0.193
1024	0.192	0.204	0.210	0.208	0.195	0.182
2048	0.189	0.209	0.206	0.203	0.207	0.193

see errata, p. 514

Maleic ~~Malic~~ *Acid, $C_2H_2(COOH)_2$*

Molecular Conductivity

V	35°	50°	65°
32	197.60	230.35	257.29
128	288.24	338.46	378.51
512	360.84	422.18	477.78
1024	384.97	451.57	514.51
2048	400.10	457.98	522.22

Temperature Coefficients

V	35°–50°		50°–65°	
	Cond. units	Per cent.	Cond. units	Per cent.
32	2.18	1.10	1.80	0.78
128	3.34	1.16	2.67	0.78
512	4.09	1.13	3.70	0.87
1024	4.44	1.15	4.20	0.93
2048	3.85	0.94	4.28	0.93

Limiting Conductivity

35° 402 50° 475 65° 544

Percentage Dissociation

V	35°	50°	65°
32	49.15	48.49	47.29
128	71.70	71.25	69.57
512	89.76	88.88	87.82
1024	95.76	95.06	94.59
2048	99.52	96.41	95.99

Dissociation Constants

V	35°	50°	65°
32	148.4	142.6	106.0
128	141.9	137.8	124.2
512	153.4	138.7	123.6
1024	211.1	178.6	161.5
2048	...	126.4	121.1

Fumaric Acid, $C_2H_2(COOH)_2$

Molecular Conductivity

V	35°	50°	65°
32	65.66	75.19	82.75
128	120.9	137.88	152.14
512	209.3	237.9	262.94
1024	257.9	294.2	325.09
2048	317.6	361.4	396.63

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
32	0.63	0.90	0.50	0.67
128	1.12	0.92	0.95	0.68
512	1.80	0.91	1.70	0.69
1024	2.42	0.94	2.05	0.70
2048	2.92	0.91	2.34	0.65

Limiting Conductivity

35° 402 50° 475 65° 544

Percentage Dissociation

V	35°	50°	65°
32	16.33	15.83	15.21
128	30.07	29.02	27.96
512	52.06	50.08	48.33
1024	64.15	61.93	59.75
2048	79.00	76.08	72.91

Dissociation Constants

V	35°	50°	65°
32	9.9	9.3	8.5
128	10.1	9.3	8.5
512	11.0	9.2	8.8
1024	11.2	9.8	8.6
2048	14.5	11.8	9.5

Itaconic Acid, $HOOCC(:CH_2)CH_2COOH$

Molecular Conductivity

V	35°	50°	65°
32	27.01	32.25	36.60
128	52.13	62.17	70.76
512	96.99	116.70	132.59
1024	129.71	153.97	175.02
2048	167.38	200.02	227.02

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
32	0.35	1.29	0.29	0.90
128	0.67	1.28	0.57	0.92
512	1.31	1.35	1.06	0.90
1024	1.62	1.24	1.40	0.91
2048	2.17	1.30	1.80	0.90

Limiting Conductivity

35° 400 50° 471 65° 537.5

Percentage Dissociation

V	35°	50°	65°
32	6.75	6.84	6.81
128	13.03	13.19	13.16
512	24.24	24.77	24.64
1024	32.42	32.68	32.55
2048	41.84	42.46	42.23

Dissociation Constants

V	35°	50°	65°
32	1.52	1.57	1.55
128	1.52	1.56	1.55
512	1.51	1.59	1.57
1024	1.51	1.54	1.53
2048	1.46	1.52	1.50

Citraconic Acid, $HOOCC(CH_3):CHCOOH$

Molecular Conductivity

V	35°	50°	65°
32	114.21	129.33	142.98
128	193.81	222.88	248.18
512	288.95	331.96	377.09
1024	823.68	382.98	431.52
2048	355.55	417.68	475.08

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
32	1.008	0.88	0.91	0.70
128	1.938	1.00	1.69	0.75
512	2.87	0.99	3.01	0.90
1024	3.62	1.10	3.24	0.84
2048	4.14	1.16	3.83	0.91

Limiting Conductivity

35° 400 50° 471 65° 537.5

Percentage Dissociation

V	35°	50°	65°
32	28.55	27.45	26.60
128	48.45	47.32	46.17
512	72.23	70.48	70.15
1024	82.17	81.31	80.28
2048	88.88	88.67	88.38

Dissociation Constants

V	35°	50°	65°
32	35.65	32.45	30.12
128	35.57	33.20	30.93
512	36.69	32.86	32.19
1024	37.06	32.79	31.91
2048	34.68	33.88	32.82

Mesaconic Acid, $HOOCC(CH_3):CHCOOH$

Molecular Conductivity

V	35°	50°	65°
32	58.04	65.94	72.66
128	108.30	123.00	135.50
512	188.40	214.10	235.30
1024	233.90	266.10	293.35
2048	278.60	318.30	352.70

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
32	0.52	0.91	0.41	0.67
128	0.98	0.90	0.83	0.68
512	1.71	0.90	1.41	0.66
1024	2.50	0.92	1.86	0.68
2048	2.64	0.95	2.29	0.72

Limiting Conductivity

35°	400	50°	471	65°	537.5

Percentage Dissociation

V	35°	50°	65°
32	14.51	13.99	13.51
128	27.07	26.11	25.20
512	47.10	45.45	43.77
1024	58.47	56.49	54.57
2048	69.65	67.57	65.61

Dissociation Constants

V	35°	50°	65°
32	7.7	7.1	6.6
128	7.8	7.2	6.6
512	8.1	7.3	6.6
1024	8.0	7.1	6.4
2048	7.8	6.9	6.1

m-*Chlorobenzoic Acid*, $C_6H_4ClCOOH$

Molecular Conductivity

V	0°	12°.5	25°	35°
512	52.37	69.79	86.91	98.72
1024	70.06	93.47	115.97	130.39
2048	92.76	120.27	149.13	169.19

Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
512	1.39	2.65	1.37	1.96	1.18	1.35
1024	1.87	2.66	1.80	1.92	1.44	1.24
2048	2.20	2.37	2.30	1.91	2.00	1.34

Limiting Conductivity

0° 222.4 12°.5 285.3 25° 350.5 35° 398.5

Percentage Dissociation

V	0°	12°.5	25°	35°
512	23.55	24.46	24.79	24.52
1024	31.50	32.76	33.08	32.72
2048	41.70	42.15	42.54	42.45

Dissociation Constants

V	0°	12°.5	25°	35°
512	1.41	1.54	1.59	1.55
1024	1.41	1.55	1.59	1.55
2048	1.45	1.49	1.53	1.52

p-*Chlorobenzoic Acid*, $C_6H_4ClCOOH$

Molecular Conductivity

V	0°	12°.5	25°	35°
2048	63.35	85.53	107.61	124.22

Temperature Coefficients

Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
1.77	2.79	1.76	2.06	1.66	1.54

Limiting Conductivity

0° 222.0 12°.5 285.2 25° 353.5 35° 400.0

Percentage Dissociation

V	0°	12°.5	25°	35°
2048	28.5	29.9	32.8	31.0

Dissociation Constants

V	0°	12°.5	25°	35°
2048	0.554	0.622	0.781	0.680

o-*Bromobenzoic Acid,* $C_6H_4BrCOOH$

Molecular Conductivity

V	0°	12°.5	25°	35°
128	95.79	116.50	133.63	144.77
512	142.60	176.40	205.30	226.44
1024	168.96	211.08	247.88	273.87
2048	183.37	233.05	277.56	311.05

Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
128	1.66	1.73	1.37	1.17	1.11	0.83
512	2.70	1.89	2.31	1.30	2.11	1.03
1024	3.37	1.99	2.94	1.39	2.59	1.04
2048	3.97	2.16	3.56	1.52	3.35	1.21

Limiting Conductivity

0° 223 12°.5 286.5 25° 352.4 35° 401

Percentage Dissociation

V	0°	12°.5	25°	35°
128	43.40	40.66	37.91	36.04
512	63.94	61.57	58.25	56.46
1024	75.76	73.67	70.34	68.29
2048	82.22	81.34	78.76	77.56

Dissociation Constants

V	0°	12°.5	25°	35°
128	25.99	21.76	18.08	15.86
512	22.14	19.26	15.87	14.29
1024	23.13	20.12	16.29	14.36
2048	18.56	17.32	14.26	13.08

m-*Bromobenzoic Acid,* $C_6H_4BrCOOH$

Molecular Conductivity

V	0°	12°.5	25°	35°
512	50.71	67.80	84.62	97.36
1024	69.42	92.71	115.22	131.78
2048	89.28	121.01	150.72	173.46

Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
512	1.36	2.68	1.34	1.97	1.27	1.50
1024	1.86	2.67	1.80	1.94	1.65	1.43
2048	2.53	2.83	2.37	1.95	2.27	1.50

Limiting Conductivity

0° 222.8 12°.5 285 25° 352.6 35° 401.6

Percentage Dissociation

V	0°	12°.5	25°	35°
512	22.76	23.78	23.99	24.24
1024	31.15	32.52	32.67	32.81
2048	40.07	42.45	42.74	43.19

Dissociation Constants

V	0°	12°.5	25°	35°
512	1.31	1.44	1.47	1.51
1024	1.37	1.53	1.54	1.56
2048	1.31	1.52	1.55	1.60

m-*Hydroxybenzoic Acid*, HOC_6H_4COOH

Molecular Conductivity

V	0°	12°.5	25°	35°
32	9.71	12.98	16.12	18.38
128	19.51	25.92	32.03	35.94
512	36.84	48.75	60.12	68.25
1024	50.57	66.27	81.88	93.15
2048	66.78	86.93	107.12	121.83

Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
32	0.26	2.68	0.257	1.98	0.218	1.34
128	0.51	2.62	0.489	1.88	0.389	1.21
512	0.95	2.58	0.909	1.88	0.812	1.34
1024	1.26	2.48	1.248	1.88	1.127	1.37
2048	1.61	2.41	1.615	1.84	1.470	1.36

Limiting Conductivity

0° 219.7 12°.5 285.8 25° 350.8 35° 397.3

Percentage Dissociation

V	0°	12°.5	25°	35°
32	4.41	4.54	4.59	4.62
128	8.87	9.07	9.13	9.04
512	16.77	17.06	17.13	17.17
1024	23.01	23.18	23.34	23.44
2048	30.34	30.41	30.53	30.66

Dissociation Constants

V	0°	12°.5	25°	35°
32	0.63	0.67	0.69	0.69
128	0.67	0.70	0.71	0.70
512	0.65	0.68	0.69	0.69
1024	0.67	0.68	0.69	0.70
2048	0.64	0.64	0.64	0.66

m-*Acetoxybenzoic Acid*, $CH_3COOC_6H_4COOH$

Molecular Conductivity

V	0°	12°.5	25°	35°
128	25.89	34.52	42.71	48.69
512	48.77	64.61	79.78	90.90
1024	65.63	86.72	106.97	122.11
2048	85.45	112.34	138.66	156.64

Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
128	0.69	2.66	0.65	1.88	0.59	1.38
512	1.26	2.58	1.21	1.87	1.11	1.39
1024	1.68	2.55	1.62	1.86	1.51	1.39
2048	2.15	2.51	2.10	1.86	1.80	1.29

Limiting Conductivity

0° 220.4 12°.5 284 25° 349.1 35° 397

Percentage Dissociation

V	0°	12°.5	25°	35°
128	11.24	12.15	12.23	12.26
512	22.12	22.75	22.85	22.89
1024	29.77	30.53	30.64	30.75
2048	38.76	39.55	39.71	39.45

Dissociation Constants

V	0°	12°.5	25°	35°
128	1.11	1.31	1.33	1.38
512	1.22	1.30	1.32	1.32
1024	1.23	1.31	1.32	1.33
2048	1.19	1.26	1.27	1.25

o-*Sulphobenzoic Acid*, $HOOCC_6H_4SO_3H$

Molecular Conductivity

V	0°	12°.5	25°	35°
32	226.09	290.63	352.91	401.70
128	236.11	304.14	369.64	421.86
512	251.85	325.13	394.95	452.16
1024	256.41	330.96	401.81	454.20
2048	274.01	356.24	428.67	....

Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
32	5.16	2.28	4.98	1.71	4.88	1.38
128	5.44	2.30	5.24	1.72	5.22	1.41
512	5.86	2.32	5.58	1.71	5.72	1.44
1024	5.96	2.32	5.67	1.71	5.23	1.30
2048	6.57	2.39	5.79	1.62	..	..

Limiting Conductivity

0° 220 12°.5 284.5 25° 349.5 35° 397.5

Percentage Dissociation and *Dissociation Constants* could not be calculated because of the strength of this acid.

m-*Sulphobenzoic Acid*, $HOOCC_6H_4SO_3H$

Molecular Conductivity

V	0°	12°.5	25°	35°
512	103.67	138.58	174.18	202.11
1024	119.54	159.75	200.06	231.98
2048	135.98	181.68	227.20	262.67

Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
512	2.79	2.69	2.84	2.04	2.79	1.60
1024	3.21	2.68	3.22	2.01	3.19	1.59
2048	3.65	2.68	3.64	1.99	3.54	1.55

Limiting Conductivity

0° 220 12°.5 284.5 25° 349.5 35° 397.5

Percentage Dissociation

V	0°	12°.5	25°	35°
512	47.12	48.71	49.83	50.84
1024	54.33	56.15	57.24	58.35
2048	61.80	63.85	65.00	66.08

Dissociation Constants

Too strong to give a constant.

Picric Acid, $C_6H_2(NO_2)_3OH$

Molecular Conductivity

V	0°	15°	25°	35°	50°	65°
32	193.0	260.0	303.4	345.1	402.0	456.2
128	201.1	272.5	320.0	365.2	433.3	485.1
512	207.4	280.4	328.9	377.5	449.3	501.2
1024	206.6	281.7	331.8	379.9	455.2	507.1
2048	203.5	276.8	325.9	372.7	441.4	503.2

Temperature Coefficients (Cond. Units)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65
32	4.46	4.34	4.17	3.79	3.61
128	4.76	4.75	4.52	4.54	3.45
512	4.86	4.85	4.86	4.79	3.46
1024	4.00	5.01	4.81	5.12	3.46
2048	4.88	4.91	4.68	4.58	3.44

Temperature Coefficients (Per Cent.)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
32	2.31	1.66	1.36	1.09	0.90
128	2.36	1.74	1.41	1.22	0.79
512	2.34	1.72	1.47	1.27	0.77
1024	2.42	1.77	1.44	1.34	0.75
2048	2.39	1.77	1.43	1.22	0.76

Limiting Conductivity

0° 207 15° 281.6 25° 331 35° 380 50° 451.6 65° 506.8

Percentage Dissociation

V	0°	15°	25°	35°	50°	65°
32	93.23	92.32	91.66	90.8	89.0	90.0
128	97.14	96.76	96.67	96.1	95.9	95.7
512	100.0	99.57	99.36	99.4	99.4	98.8
1024	100.0	100.0	100.0	100.0	100.0	100.0
2038	100.0	100.0	100.0	100.0	100.0	100.0

Dissociation Constants

Too strong to give a constant.

Gallic Acid, $C_6H_2(OH)_3COOH.H_2O$

Molecular Conductivity

V	0°	25°	35°	50°	65°
64	9.80	16.92	19.46	23.28	26.19
128	14.00	23.70	27.22	33.09	36.64
512	28.92	48.31	55.24	67.58	75.54
1024	37.87	62.56	71.20	86.15	95.96
2048	51.53	85.10	96.82	112.36	124.15

Temperature Coefficients (Cond. Units)

V	0°–25°	25°–35°	35°–50°	50°–65°
64	0.28	0.25	0.25	0.19
128	0.39	0.35	0.38	0.24
512	0.77	0.69	0.82	0.53
1024	0.98	0.86	0.99	0.65
2048	1.34	1.17	1.04	0.79

Temperature Coefficients (Per Cent.)

V	0°–25°	25°–35°	35°–50°	50°–65°
64	2.90	1.50	1.30	0.81
128	2.78	1.48	1.41	0.71
512	2.68	1.43	1.49	0.80
1024	2.60	1.38	1.40	0.76
2048	2.60	1.37	1.07	0.70

Limiting Conductivity

0°	25°	35°	50°	65°
220	348	396	459.1	514.3

Percentage Dissociation

V	0°	25°	35°	50°	65°
64	4.45	4.86	4.91	5.07	5.09
128	6.36	6.81	6.87	7.20	7.12
512	13.14	13.88	13.94	14.72	14.66
1024	17.21	17.97	17.97	18.76	18.63
2048	23.42	24.45	24.44	24.47	24.13

Dissociation Constants

V	0°	25°	35°	50°	65°
64	0.32	0.38	0.39	0.42	0.42
128	0.33	0.38	0.39	0.42	0.42
512	0.38	0.43	0.44	0.49	0.41
1024	0.34	0.38	0.38	0.42	0.42
2048	0.34	0.38	0.38	0.39	0.37

p-*Aminobenzenesulphonic Acid*, $H_2NC_6H_4SO_3H$

Molecular Conductivity

V	0°	12°.5	25°	35°
32	61.42	88.45	119.42	146.04
128	77.91	112.51	152.52	187.36
512	104.86	149.36	199.06	241.34
1024	122.65	169.90	226.13	272.32
2048	132.15	182.98	239.16	285.99

Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
32	2.16	3.51	2.47	2.79	2.66	2.22
128	2.76	3.53	3.20	2.84	3.48	2.28
512	3.56	3.39	3.97	3.65	4.22	2.11
1024	3.70	3.01	4.50	2.64	4.61	2.03
2048	4.06	3.07	4.49	2.45	4.68	1.95

Limiting Conductivity

0° 221 12°.5 285 25° 350 35° 398

Percentage Dissociation

V	0°	12°.5	25°	35°
32	27.79	31.03	34.12	36.69
128	35.25	39.47	43.57	47.07
512	47.44	52.40	56.87	60.63
1024	55.49	59.61	64.60	68.42
2048	59.79	64.20	68.33	71.85

Dissociation Constants

Too strong to give a constant.

o-*Toluic Acid*, $CH_3C_6H_4COOH$

Molecular Conductivity

V	35°	50°	65°
512	88.44	96.41	102.41
1024	116.70	127.31	134.94
2048	154.70	168.46	177.70

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
512	0.53	0.60	0.40	0.41
1024	0.71	0.60	0.51	0.40
2048	0.91	0.59	0.62	0.36

Limiting Conductivity

35° 397 50° 470.1 65° 536

Percentage Dissociation

V	35°	50°	65°
512	22.20	20.50	19.10
1024	29.47	27.29	26.10
2048	39.16	35.83	33.15

Dissociation Constants

V	35°	50°	65°
512	1.25	1.03	0.88
1024	1.30	1.00	0.90
2048	1.22	0.98	0.80

m-*Toluic Acid*, $CH_3C_6H_4COOH$

V	35°	50°	65°
512	61.95	71.29	78.44
1024	84.03	98.70	108.33
2048	112.8	128.87	140.90

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
512	0.60	1.00	0.48	0.65
1024	0.97	1.04	0.64	0.65
2048	1.07	0.95	0.80	0.62

Limiting Conductivity

35° 397 50° 470.4 65° 541.9

Percentage Dissociation

V	35°	50°	65°
512	15.60	15.15	14.47
1024	21.16	20.99	19.99
2048	28.41	27.41	26.00

Dissociation Constants

V	35°	50°	65°
512	0.56	0.52	0.47
1024	0.55	0.54	0.48
2048	0.55	0.51	0.45

p-*Toluic Acid*, $CH_3C_6H_4COOH$

V	35°	50°	65°
512	55.54	62.98	68.37
1024	75.23	86.30	95.43
2048	102.96	114.93	125.35

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
512	0.50	0.90	0.36	0.57
1024	0.74	0.98	0.61	0.69
2048	0.80	0.77	0.69	0.60

Limiting Conductivity

35° 397 50° 469.1 65° 538.8

Percentage Dissociation

V	35°	50°	65°
512	13.98	13.42	12.68
1024	18.94	18.39	17.71
2048	25.93	24.49	23.26

Dissociation Constants

V	35°	50°	65°
512	0.44	0.40	0.35
1024	0.43	0.40	0.37
2048	0.44	0.38	0.34

Mandelic Acid, $C_6H_5CH(OH)COOH$

Molecular Conductivity

V	35°	50°	65°
8	22.40	25.76	28.62
32	43.60	50.07	55.40
128	82.32	94.42	104.47
512	146.07	168.20	185.86
1024	188.60	216.03	239.36
2048	234.20	268.62	298.03

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	0.22	1.00	0.19	0.74
32	0.43	0.99	0.35	0.71
128	0.81	0.98	0.67	0.71
512	1.47	1.01	1.18	0.70
1024	1.83	0.97	1.55	0.72
2048	2.29	0.98	1.96	0.73

Limiting Conductivity

35° 397 50° 475.4 65° 539.9

Percentage Dissociation

V	35°	50°	65°
8	5.64	5.41	5.30
32	10.98	10.52	10.25
128	20.73	19.84	19.34
512	36.79	35.35	34.41
1024	47.50	45.40	44.32
2048	58.99	56.46	55.19

Dissociation Constants

V	35°	50°	65°
8	4.26	3.86	3.71
32	4.23	3.86	3.66
128	4.23	3.83	3.62
512	4.18	3.78	3.53
1024	4.19	3.69	3.45
2048	4.14	3.54	3.32

Sebacic Acid, $C_8H_{16}(COOH)_2$

Molecular Conductivity

V	0°	12°.5	25°	35°
512	Precipitated	Precipitated	37.95	42.38
1024	34.27	44.28	53.00	59.43
2048	46.42	59.40	71.19	79.60

Temperature Coefficients

	0°–12°.5		12°.5–35°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
512	..	..	..	..	0.35	0.92
1024	0.80	2.33	0.69	1.55	0.51	0.96
2048	1.04	2.24	0.94	1.58	0.65	0.91

Limiting Conductivity

0°	218	12°.5	284	25°	343.5	35°	391

Percentage Dissociation

V	0°	12°.5	25°	35°
512	...	...	11.04	10.83
1024	15.72	15.59	15.43	15.19
2048	21.29	20.91	20.72	20.35

Dissociation Constants

V	0°	12°.5	25°	35°
512	...	...	2.6	2.5
1024	2.8	2.8	2.7	2.6
2048	2.8	2.6	2.6	2.5

The following acids were tested but were found to be either too slightly soluble to work with, or to undergo decomposition:

Nitrocinnamic acid (insoluble).

β-Naphtholdisulphonic acid (insoluble).

Terephthalic acid (insoluble).

Aminosalicylic acid (insoluble).

Aminophenolsulphonic acid (decomposed).

p- and *o*-Nitro- and dinitrophenols were studied, but the conductivities found were so small that the results were not reliable, since the percentage error due to unavoidable experimental errors was relatively large.

Dissociation Constants

	0°	12°.5	25°	35°	50°	65°
m-Chlorobenzoic	1.41	1.52	1.57	1.54	..	..
p-Chlorobenzoic	0.55	0.62	0.78	0.68	..	..
o-Bromobenzoic*	..	..	..	..	..	..
m-Bromobenzoic	1.33	1.49	1.52	1.55	..	..
m-Hydroxybenzoic	0.65	0.67	0.68	0.69	..	..
m-Acetoxybenzoic	1.19	1.29	1.41	1.32	..	..
o-Sulphobenzoic*	..	..	..	..	..	..
m-Sulphobenzoic*	..	..	..	..	..	..
Picric*	..	..	..	..	..	..
Gallic	0.36	..	0.38	0.39	0.42	0.40
Aminobenzenesulphonic*	..	..	..	..	..	..
o-Toluic*	..	..	..	1.25	1.00	0.88
m-Toluic*	..	..	..	0.55	0.52	0.46
p-Toluic*	..	..	..	0.44	0.39	0.35
Mandelic*	..	..	..	4.2	3.7	3.5
Sebacic	2.8	2.7	2.6	2.5	..	..

	0°	12°.5	25°	35°	50°	65°
Butyric*	...	...	...	0.140	0.131	0.118
Isobutyric*	...	...	...	0.114	0.121	0.122
Malic	4.28	4.67	4.81	5.00	....	....
Pyrotartaric	0.88	0.85	0.83	....	....	....
Racemic*	...	...	...	....	....	....
Hippuric	2.11	2.20	2.27	2.23	2.32	2.23
Citric*	...	...	...	....	....	....
Aconitic*	...	...	...	....	....	....
Crotonic	0.193	0.206	0.210	0.208	0.023	0.188
Maleic*	...	...	...	....	....	....
Fumaric*	...	...	...	11.3	9.8	8.8
Itaconic*	...	...	...	1.50	1.55	1.54
Citraconic*	...	...	...	35.8	32.9	31.5
Mesaconic*	...	...	...	7.8	7.1	6.4

In the preceding table those values which were omitted have been determined by other investigators in this laboratory. This applies chiefly to the acids whose values at only the higher temperatures are given. The acids that we have studied only at lower temperatures are now being studied at the higher temperatures by others working in this laboratory.

It has been shown by the work of Ostwald and Jones, and others in this field, that the Ostwald dilution law does not hold for strongly dissociated acids. The "constants" of acids of this class have been omitted. In the tables that were secured in the experimental work, it frequently happens that irregular constants are given. These are of value only in that they enable us to determine the relative strengths of such acids.

It had been observed by those who had already worked in this laboratory that as a rule the percentage dissociations of the organic acids decreased with rise in temperature. They noted that the values of percentage dissociation of certain acids increased with rise in temperature. In our work, however, we have found that in each case the increase has been at a diminishing rate. As we went further with the study of the acids, we found that we have in all cases reached the maximum dissociation, with the exception of citric acid.

Springer,[1] working on this problem, had shown that the maximum dissociation was reached in every case studied by him, except for the amino acids, such as sulphanilic, metanilic, naphthionic and dinitroaminophenol. In our work we have not studied acids of this class; but certain groups of those with which we have worked show an increase in dissociation over a wide range in temperature. The acids that show this property to the greatest extent are those containing the hydroxy (OH) group. These acids have percentage dissociation values which increase, attain a maximum, and then decrease.

The temperature coefficients of conductivity, expressed in conductivity units, for all of the above acids show an increase with the dilution of the solution, and a decrease with rise in temperature. As we would expect, the rate of increase or decrease varies greatly. There seems to be a relation between the strength of the acid and the rate of increase or decrease of the temperature coefficients of conductivity with rise in temperature. The stronger the acid, the less rapid is the change. This is obvious from the fact that strong acids are so largely dissociated at all dilutions that a change in the dilution would change the coefficients very slightly.

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[1] This Journal, **48**, 411 (1912).

The temperature coefficients of conductivity of acids, even of mineral acids to a certain extent, decrease with rise in temperature. The literature shows also that the mineral acids are more or less hydrated in solution. It is evident that an acid which is either unhydrated or only slightly hydrated (as is the case with most of the organic acids studied in this investigation) would show a rapid decrease in the temperature coefficients of conductivity with rise in temperature; since there would be no complex, hydrated ion to lose water, and, thus, from this cause, the conductivity could not be increased.

In the following table are given results which illustrate this point:

Weak Unhydrated Acids

Temperature Coefficients of Conductivity at V = 1024

	35°–50°	50°–65°
Butyric	0.019	0.013
Isobutyric	0.015	0.009
Pyrotartaric	0.12	0.11

The following table is from the work of Jones and Wightman.[1]

In this table are found the similar values for some of the hydrated acids. There are, in addition to the four strong acids in this table, also two weaker acids—racemic and citric—and these show the same decrease in the coefficients as the strong acids.

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[1] THIS JOURNAL, **46**, 56 (1911).

Acid	Water of cryst. H_2O	0°–15°	15°–25°	25°–35°	Decrease in per cent.
Meconic	3	10.06	9.94	9.18	8.8
Benzenesulphonic	1	5.26	5.05	5.06	3.8
p-Toluenesulphonic	4	4.92	4.84	4.67	5.3
1,2,4-Nitrotoluenesulphonic	2.5	4.74	4.67	4.35	8.2
Racemic $K_0° = 9.1$	1	3.76	3.56	3.43	8.0
Citric $K_0° = 6.85$	1	3.64	3.59	3.38	7.1

This indicates that the strength of the acid has very little to do with the gradual decrease in temperature coefficients, but that this decrease is caused by hydration; and the above relation applies to the strong acids only because they are the acids which are the most strongly hydrated.

This same relation holds in our work. The temperature coefficients of conductivity of the acids are larger for stronger acids. This is shown by the following tables, in which the acids are arranged according to their strengths:

Temperature Coefficients, 35°–50°, $V = 1024$

	Cond. units	K
Isobutyric	0.316	0.114
Crotonic	0.54	0.208
Itaconic	1.62	1.55
Mandelic	1.83	4.2
o-Sulphobenzoic	5.12	100 per cent. diss.

All the work done in this laboratory on the conductivity of organic acids has shown that the temperature coefficients of conductivity, expressed in percentage, decrease slightly with increasing dilution, and more rapidly with rise in temperature. The decrease due to rise in temperature manifests itself in every case studied, but a large number of exceptions present themselves in the decrease due to increasing dilution. No doubt this is the result of hydrolysis.

In all the acids that we have studied, the percentage temperature coefficients of conductivity are small and are of the same order of magnitude. The decrease is regular as the temperature rises. This indicates that some constant factor has influenced the solution,[1] such as the viscosity of the medium.

The study of isomeric acids has always been of interest, and they have been the subject of a large amount of investigation. Ostwald,[1] Walker[2] and Derrick[3] have worked on the correlation of ionization and structure for such acids, and on the effect of substitution.

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[1] Jones and West: This Journal, **34**, 418 (1905).

Our work has confirmed the following statement of Springer and Jones:

"In the case of isomeric acids containing two carboxyl groups, the acid with these groups in the 'ortho' or the 'cis' position is always the stronger."

o-Toluic 35°, $K = 1.25$
m-Toluic 35°, $K = 0.55$
p-Toluic 35°, $K = 0.44$
o-Bromobenzoic 35°, too strong an acid to give a constant
m-Bromobenzoic 35°, $K = 1.55$
Maleic (cis) 35°, $K = 154$
Fumaric (trans) 35°, $K = 11.3$
Citraconic (cis) 35°, $K = 35.8$
Mesaconic (trans) 35°, $K = 7.8$

Euler[4] showed that the conductivity of organic acids is a parabolic function of the temperature. This was also brought out by the work of White and Jones. Wightman and Jones and Springer and Jones plotted curves, using conductivities as ordinates and temperatures as abscissas, and calculated the conductivity of a number of acids from Euler's formula:

$$\mu_t = \mu_0 + at - bt^2$$

This was always found to hold. It holds also in our work.

The dissociation of a large number of organic acids decreases with rise in temperature. As mentioned above, in certain cases the percentage dissociation apparently attains a maximum at one of the intermediate temperatures, usually at 25° or 35°. This has been observed and noted in the publications of Euler,[5] Schaller,[6] White and Jones,[7] and Wightman and Jones.[8]

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[1] Z. physik. Chem., **3**, 170 (1889).
[2] J. Chem. Soc., **61**, 605 (1892); **67**, 147 (1895).
[3] J. Am. Chem. Soc., **33**, 1881 (1911); **34**, 74 (1912).
[4] Z. physik. Chem., **21**, 257 (1896).
[5] *Ibid.*, **21**, 247 (1896).
[6] *Ibid.*, **25**, 497 (1898).
[7] This Journal, **44**, 196 (1910).
[8] *Ibid.*, **46**, 56 (1911).

Thus far no one has offered a satisfactory explanation. The problem is not simple, there being many factors, any one of which might greatly influence the dissociation. As is well known, decrease in the association of the solvent and in its dielectric constant would greatly affect the conductivity. The effect of rise in temperature has been shown to diminish both the association and the dielectric constant of the solvent. The nature of the dissolved substance itself plays, of course, no small role in the effect on the conductivity of its solution.

Wightman and Jones and Springer and Jones, and we ourselves, tested the following formulas:

"A more general, though empirical equation for calculating the constants was suggested by Storch, and employed by Bancroft, Noyes, and others, viz.:

$$K = C_i^n / C_s$$

in which $C_i = \alpha / V$ denotes the volume concentration of the dissociated portion, and $C_s = (1 - \alpha) / V$, the volume concentration of the undissociated part; K and n are both functions of the electrolyte. By using C_i as values for the ordinates and C_s as values for the abscissae, a curve can be plotted from which it is possible to obtain n. The values for n found by previous workers, for a large number of salts and acids, vary from 1.36 to 1.55.

"We have attempted, by means of this method, to obtain constants for the strong acids, but the equation did not seem to be applicable.

"Further work on the organic acids, and also on the organic bases, both in aqueous and in nonaqueous solutions, and through a wider range of temperature, is being carried out in this laboratory."

The following tables show the agreement in the results in the case of a few acids studied by two investigators. The examples were chosen at random and are typical:

Maleic Acid, 35°

V	White and Jones	Smith and Jones
32	198.8	197.6
1024	384.6	384.97
2048	400.8	400.10

Gallic Acid, 35°

V	White and Jones	Smith and Jones
64	19.36	19.46
1024	71.18	71.20
2048	96.7	96.82

Hippuric Acid, 25°

V	Ostwald	Smith and Jones
128	54.3	55.16
1024	131.1	133.96

m-*Hydroxybenzoic Acid, 25°*

V	Ostwald	Smith and Jones
32	18.18	18.38
512	67.90	68.24
1024	91.63	93.155

Gallic Acid, 25°

V	Ostwald	Smith and Jones	White and Jones
64	16.83	16.92	16.90
512	47.74	48.31	48.33
1024	66.53	62.56	62.50
2048	...	85.10	85.02

Malic Acid, 25°

V	Ostwald	Smith and Jones
128	71.52	78.46
512	128.1	132.70
1024	166.6	172.50
2048	213.0	211.16

Summary

Most of the relations previously established by Jones and his coworkers have been confirmed in this investigation. The mere statement of some of these relations is sufficient, since a glance at the data alone will show that they hold.

1. The temperature coefficients of conductivity increase rapidly with dilution, and decrease rapidly with rise in temperature for the weak organic acids. However, if the acids are hydrated, the temperature coefficients of conductivity are larger and the rate of increase or decrease just mentioned is much slower. The stronger the organic acid, the larger these units.

2. The percentage temperature coefficients of conductivity are small, are of the same order of magnitude, and decrease with rise in temperature.

3. The conductivity of most organic acids is a parabolic function of the temperature, as has been pointed out by Euler. His formula

$$\mu_t = \mu_0 + at - bt^2$$

has been shown to hold in every case.

4. The relative strength of organic acids is not dependent upon the temperature.

5. "There is no general statement possible concerning the change in dissociation of the organic acids with change in temperature. Maxima occur with several between 25° and 35°, while in other cases maxima are indicated at slightly higher temperatures than those at which measurements were made. The dissociation of several acids decreases regularly from 0°."

6. Isomeric acids do not behave similarly with regard to change in their dissociation.

7. Strong organic acids, as is well known, do not obey the Ostwald dilution law.

8. The "ortho" and "cis" forms of isomeric acids are the stronger, i. e., have the larger constants.

9. The migration velocities of the anions present are functions of the number of atoms that are present in them. As has been already pointed out in this paper, this fact was made use of in determining the μ_∞ values of dibasic acids.

10. Most dibasic acids dissociate like monobasic acids.

11. "The behavior of the organic acids with respect to the change of their dissociation with the temperature is not in accord with the hypothesis of Thomson-Nernst, which connects dissociating power and dielectric constants; or at least the influence of some other unknown factor is suggested."

Chemical Laboratory
Johns Hopkins University
May, 1913

THE RADIUM CONTENT OF SOME ALABAMA COALS

By Stewart J. Lloyd and John Cunningham

Since the discovery in recent years that practically all rocks and most waters contain measurable quantities of radium and that this radium is continually giving off heat to its surroundings while undergoing transformation into helium, and probably lead, several of the classic problems of geology have been reopened and re-examined in the light of these additional facts. The probable age of the earth, determined in the past by palaeontological, stratigraphical and physical considerations, as well as by a study of the sodium content of the oceans and rivers, has been redetermined by Strutt,[1] Holmes and others from the uranium : helium and the uranium : lead ratio in rocks and minerals, with results indicating a much higher antiquity than had been previously suspected. The earth's internal heat, generally attributed to the uncooled interior postulated by the Laplacian hypothesis of the earth's origin, has been accounted for with embarrassing fullness[2] by the radium present in the earth, a fact which lends no little support to the planetesimal alternative. Even vulcanism and the complex phenomena of mountain building[3] have been subjected to renewed scrutiny with a view to the possible connection between them and the presence of radium in the earth, while the therapeutic value of springs and a host of minor phenomena have been attributed to its presence.

It is obvious that an accurate knowledge of the radium content of our rocks and waters is necessary before any final conclusions can be drawn as to the part played by radium and radioactive processes in geological phenomena. Numerous examinations have already been made of rocks, springs, rivers, lakes and of sea water, but it cannot be said that the results are even fairly satisfactory. The values for sea water, for instance, as given by Joly[4] and by Eve[5] are far apart, one being twenty times the other. The two methods used for the determination of radium in siliceous rocks, the ordinary solution process with sodium carbonate so common in silicate analysis and the recent fusion method of Joly,[1] do not agree, the latter usually giving higher, but sometimes lower, results.[2] Moreover, there has been no attempt, save in a few cases, to obtain representative samples of rocks, picked hand specimens being usually employed. It is the firm conviction of the writers that the fundamental data for the geological side of radioactivity have not yet been determined with any degree of accuracy and that a complete resurvey of the field must be made before final conclusions can legitimately be drawn.

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[1] P. Roy. Soc., A, **85**, 248 (1911); **76**, 95 (1905); **84**, 379 (1911).

[2] Rutherford: "Radioactivity," 2nd Edition, p. 494; "Radioactive Substances and Their Radiations," p. 648.

[3] Joly: "Radioactivity and Geology," p. 140.

[4] Joly: Phil. Mag., **15**, 385 (1908); **18**, 396 (1909).

[5] Eve: *Ibid.*, **18**, 102 (1909).

With this in view a comprehensive examination for radium of the rocks, minerals and waters of the state of Alabama has been begun, the first results of which are given in this paper. The Alabama Geological Survey has been making an analytical study of the various coals of the state, the samples for which were taken in the standard method with exceptional care, so that they may confidently be considered as representative of the seams from which they come. Through the courtesy of the Survey officials these samples were made available for use, and the determinations given in this paper, with the exception of that of the lignite, were made on them exclusively. To bring the material into a form suitable for the measurement of its emanation and hence of its radium content, use was made of a method not hitherto employed for this purpose. The great disadvantage of the solution method is the necessity of using large quantities of sodium carbonate, which frequently contains small amounts of radium, and which has to remain in the resulting solution, rendering it heavy and difficult to boil. The formation of a precipitate in this new method, however, has not led, in the authors' experience, to any difficulty in obtaining the complete amount of emanation, despite Joly's statement.[3] Radium carried down in any precipitate, such as barium sulphate, becomes entirely normal in its emanating power upon continued heating and stirring, and accurate results may be obtained in two or three successive determinations.[1] The fusion method was not used as it did not appear to be suitable for coals, and in any event experience with minerals has shown that considerable amounts of emanation are lost even before grinding.[2] The actual determinations were made in the following manner:

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[1] Phil. Mag., **22**, 134 (1911).

[2] Rutherford: "Radioactive Substances and Their Radiations," p. 647.

[3] "Radioactivity and Geology," p. 264.

Forty grams or more of the coal, ground to 100 mesh, were heated in a platinum dish until all the carbonaceous matter was removed. The residue, mostly silica, was then treated with dilute hydrofluoric acid and gently heated. Most of the solid matter disappeared, and hydrochloric acid was then added, which usually dissolved the remainder entirely. The small unattacked residue still remaining in one or two cases was fused with acid potassium sulphate and the resulting solution added to the main one. The addition of sulphates does *not* lessen the emanating power of the radium, if the solution is kept at the boiling temperature for an hour or more, or if two successive determinations are made.[2] With some of the coals, which contained a little lime, small precipitates of calcium fluoride were formed. These do not affect the emanating power of radium, nor does the presence of hydrofluoric acid.[1]

The electroscope used was of the ordinary vacuum type, but with exceptionally fine amber insulation. For standardizing, a very dilute solution in nitric acid of Joachimsthal pitchblende containing 46.2 per cent. of uranium was employed, so that the quantity of radium with which the instrument was standardized was of the same order of magnitude as that in the samples. The method of transferring the emanation from the solution to the electroscope was essentially that described by McCoy,[2] save that the emanation was collected over a warm saturated solution of sodium chloride. It was assumed, following Rutherford, that one gram of uranium is in equilibrium with 3.4×10^{-7} gram of radium.

[1] Lloyd: J. Phys. Chem., **14**, 476 (1910).

[2] McCoy and Ross: J. Am. Chem. Soc., **29**, 1701 (1907).

No.	Mine	Locality	Weight of coal, grams	Per cent. of ash	Ra per gram coal	Ra per gram ash
1	Wadsworth	Falliston				
	Red Ash	Cahaba Field	40.3	4.3	0.0475	1.10
2	Mary Lee	Warrior Field	45.4	16.13	0.34	2.19
3	Pratt No. 5	Warrior Field	56.7	4.94	0.37	7.05
4	Blocton	Cahaba Field	53.5	6.52	0.27	4.39
5	Coalmont	Cahaba Field	49.0	8.9	0.086	0.95
6	Pratt No. 3	Warrior Field	59.2	6.21	0.088	1.41
7	Galloway	Warrior Field	120.6	10.67	0.34	2.95
8	Corona	Warrior Field	384.3	9.56	0.054	0.57
9	Conners-Weyman	Falliston Cahaba Field	102.8	6.89	0.0475	0.69
10	Little Cahaba	Cahaba Field	96.3	6.57	0.028	0.51
11	Lignite	Pike Co.	81.6	11.36	0.15	1.34
				Average,	0.166	2.15

The above table contains the data obtained. The samples in every case were allowed to stand for thirty days before measuring, so that the maximum amount of emanation might accumulate, as the amounts were small enough even then. The weights of radium are expressed, following the usual custom, as multiples of 10^{-12}.

So far as we have been able to ascertain no results of other examinations of coals for radium have been published, so that comparisons cannot at present be made. Determinations of the sulphur content and of the volatile and fixed carbon in all of these samples have been made and will be published later by the Alabama Geological Survey, but there appears to be no connection between these figures and the radium content. The average per gram of ash, 2.15×10^{-12}, is distinctly higher than the average for sedimentary rocks as determined by Fletcher,[1] who gives the following table:

Coarse detrital sediments	1.5
Metamorphosed coarse detrital sediments	1.5
Fine detrital sediments (argillaceous)	1.3
Fine detrital sediments (schistose)	1.1
Calcareous sediments	0.8

The great range of variation in the amount of radium per gram of ash is rather remarkable, the lowest being roughly one-fifteenth of the highest. As is seen from the above table, the sedimentary rocks do not vary much in their radium content, a range of about one to two being shown, so that the much greater variation in the coals must be due to a specific tendency on the part of certain plants to secrete exceptionally large amounts of radium. No examinations for radium of the ash of plants have been made, so far as the literature shows, though the results of such an investigation would be of considerable interest.

UNIVERSITY OF ALABAMA
June, 1913

[1] Phil. Mag., **23**, 279 (1912).

REVIEWS

Jahrbuch der organischen Chemie. Von Professor Dr. Julius Schmidt, Stuttgart. VI. Jahrgang: Die Forschungsergebnisse und Fortschritte im Jahre 1912. Leipzig: Johannes Wörner's Verlag. 1913. pp. xiv + 268. Preis: brosch., M. 12.80; geb., M. 14.30.

This excellent publication will as usual give chemists an opportunity to review the work of the preceding year. Notwithstanding the great activity in other fields of chemistry there is still much valuable work done in organic chemistry and this is likely to continue as long as man retains his inquiring tendencies. The scope of the subject is constantly growing wider and the number of problems calling for solution is increasing to at least an equal extent. To be sure, the nature of the problems under investigation is changing. The determination of the structure of compounds is no longer the principal occupation of organic chemists as it was a generation and more ago. And the synthesis of compounds occurring in nature now requires greater mental power and mechanical skill and is therefore not as freely indulged in as formerly. But problems in structural and synthetical chemistry, more difficult than those that were first taken up, remain to be solved, and some of these are receiving the attention of master workers. Witness the work of Fischer, Abderhalden, Kossel and others on the proteins; that of Willstätter and Marchlewski on chlorophyll; that of Harries on India rubber; that of E. Fischer on tannin, etc.

Every chemist would be benefited by a careful examination of this volume, especially those who have been carried away by strong currents in other directions and have lost sight of what they sometimes call old-fashioned organic chemistry.

The statements concerning the articles referred to are unusually clear. I. R.

Theorien der organischen Chemie. Zugleich zweite Auflage der neueren theoretischen Anschauungen auf dem Gebiete der organischen Chemie. Von Dr. Ferdinand Henrich, A. O. Professor an der Universität Erlangen. Mit 13 Abbildungen im Text. Braunschweig: Druck und Verlag von Friedr. Vieweg & Sohn. 1912. pp. xix + 402. Preis: geh., M. 10; geb., M. 11.

The first edition of this book was favorably noticed in This Journal at the time of its publication.[1] The new edition appears under a new and broader title. In regard to it the author says: "In erster Linie soll das Buch dem Studierenden eine Einführung in die Theorien der organischen Chemie geben und ihm den Kontakt mit der Literatur ergmöglichen. Dann soll es dem auf der Höhe stehenden Fachmann ein Nachschlagebuch sein, durch das er sich rasch über seltener vorkommende Theorien und Begriffe orientieren kann." The chapter on "Farbe und Constitution" has been completely rewritten. That on "Neuere elektrochemische Ansichten" has been materially enlarged. Chapters on "Substitution im Benzolkern," and on "Physikalisch-chemische Einflüsse" have been introduced.

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[1] Vol. **42**, p. 472.

The book is very clearly written and can be highly recommended. I. R.

GENERAL INDEX TO THE CHEMICAL NEWS. VOLS. I TO 100. London: Chemical News Office. 1913. pp. 712. Price, £2.

This index refers to the volumes of the Chemical News that have appeared from 1860 to 1909—half a century. Sir William Crookes, the founder and editor, is still active, although in his 82nd year, and this is a good opportunity to congratulate him upon the completion of more than fifty years of service as editor of this unique chemical journal. The writer, who has been familiar with the Chemical News for over forty years, is tempted to philosophize upon the rôle it has played and to tell of his own attitude of mind towards it at different stages of his development, but this would hardly be appropriate, as the Index is under review and not the Journal, and certainly not the writer.

The amount of work involved in the preparation of the Index must have been enormous. The anonymous laborer deserves the thanks of all who ever have occasion to consult the Chemical News. He also deserves their sympathy. In a brief preface directions for using the index are given. The author says: "The methods adopted in it are believed to be those which in the main will prove to be the most convenient and time-saving." And again, "every effort has been made to enable readers of the Chemical News to look up quickly and easily any subjects which have appeared in its pages, however fragmentary and incomplete their knowledge or recollections of them may be." I. R.

UEBUNGSBEISPIELE AUS DER UNORGANISCHEN EXPERIMENTALCHEMIE. Von HEINRICH BILTZ und WILHELM BILTZ. Zweite Auflage. Leipzig: Wilhelm Engelmann. 1913. pp. xi + 239. Price, M. 8.

This is one of the best, if not the best and most up-to-date, books on inorganic preparations, covering, as it does, a wide range of both variety of substances and in the conditions of experimentation. It should be available for use in every laboratory where inorganic preparations are made as a regular part of the training. The second edition has been improved by the introduction of changes suggested by the experiences of those who have been using the earlier edition. Not only are the conditions and methods of preparation studied, but many of the physical properties of the substances are determined. The press work is also especially attractive.

J. E. G.

INORGANIC CHEMISTRY. By HAMILTON PERKINS CADY, A.B., PH.D., Professor of Chemistry in the University of Kansas. International Chemical Series: H. P. TALBOT, PH.D., Consulting Editor. New York: McGraw-Hill Publishing Company. 1912. pp. xiv + 629. Price, $2.50.

In this volume the author has brought together a large amount of material, which he has presented in a very attractive way. The book is characterized by the introduction of somewhat more physics and physical chemistry than is usually included in elementary texts.

So far as physics is concerned, the teacher of elementary students in chemistry must either teach a certain amount of physics or presuppose a knowledge on the part of his students which they may or may not possess. It is not always safe to assume such knowledge and consequently the effort is usually made to teach certain fundamental principles of physics under rather discouraging conditions and not always with very happy results. The author has endeavored to meet the situation by inserting at intervals, necessarily in a more or less arbitrary way, matter which is purely physical, and it is not always clear that it has been done in the most logical and effective way. For example, a number of paragraphs would appear unnecessary for students who have a proper knowledge of physics and unintelligible to those who have not such knowledge.

This is not so much a criticism of the present book, perhaps, as of our educational system. The difficulties mentioned are inherent in the situation which confronts teachers of chemistry and will continue till our methods of teaching physics and chemistry are better standardized.

The amount of theory that can be successfully taught in an elementary course is bound up with this same question and depends largely upon the amount of physics which the student already knows and upon his maturity. It still remains an open question whether or not the first year might not with advantage be devoted primarily to a study of chemical reactions in the old way and to a patient accumulation of a body of facts, which will serve as a foundation upon which theory may be built up in the more advanced courses. The author evidently thinks that the principles of physical chemistry, including some theory, should be introduced at the beginning, as he discusses in the early chapters such topics as reversible reactions and equilibrium, the phase rule, vapor pressure of solutions, "constant boiling hydrochloric acid," lowering of freezing point, heat of neutralization, ionic theory, etc.

On the whole, the book is well gotten up and evidently is the result of a great deal of painstaking work. From the mechanical point of view it is distinctly pleasing; the plates are good, the arrangement excellent and there are few typographical errors. B. F. L.

MANUAL OF QUALITATIVE ANALYSIS. Reagent and Combustion Methods. By WILBUR F. HOYT, A.B., A.M., Peru State Normal School, Peru, Nebraska. New York: The Macmillan Company. 1913. pp. vi + 35. Price, 30 cents.

From reading through this small volume one is likely to conclude that the author intended it for the use of his own classes only. But two statements in the foreword indicate that he entertains more ambitious hopes. Among other topics treated is water analysis, because "some means for determining the purity of water should be given wide circulation." "Attention is called to the scope of the manual, treating, as it does, of valence, reactions, equations, qualitative analysis both by the 'wet' and 'dry' methods, sample notes, difficult equations, and a hundred confirmations of the various metals and acids usually found only in advanced and exhaustive treatises"—and all embraced within the limits of thirty-five small pages! B. F. L.

JAHRBUCH DER ELEKTROCHEMIE UND ANGEWANDTEN PHYSIKALISCHEN CHEMIE. Begründet und bis 1901 herausgegeben von PROF. DR. W. NERNST und PROF. DR. W. BORCHERS. Berichte über die Fortschritte des Jahres 1906. Herausgegeben von DR. PHIL. HEINRICH DANNEEL, Genf, und PROF. DR. JULIUS MEYER, Breslau. XIII. Jahrgang. Halle (Saale): Verlag von Wilhelm Knapp. 1913. pp. xii + 869. Price, M. 32.

The thirteenth volume of this well-known "Jahrbuch" contains 496 pages devoted to scientific and 353 to applied electrochemistry. The scientific work is discussed under the headings of: General, Conductivity and Condition in Solutions, Chemical and Electrical Energy, Polarization and Electrolysis, Electrical Phenomena in Gases, Radioactivity;

the applied part, under the headings: Production of Current, Inorganic Electrochemistry and Physical-Chemical Procedure and Products, Galvanotechnic and Related Fields, Electrolysis of Alkali Chlorides, Preparation of Hydrochloric Acid, Sulphur and Its Compounds, especially Sulphuric Acid, Contact Chemistry and the Law of Mass Action, and Apparatus for the Electrochemical Industries.

The reviews of the work done seem, on the whole, satisfactory, but are somewhat uneven in character. This is unavoidably the case.

The value of this handbook would be greatly increased if it appeared more promptly. It is now more than six years behind the researches in these fields, and some of its contents is, therefore, out of date when the book appears. Further, it would be very much more useful if it appeared more promptly.

H. C. J.

DIE ELEKTROLYTISCHE ALKALICHLORIDZERLEGUNG MIT FESTEN KATHODENMETALLEN. Von DR. JEAN BILLITER, Privatdozent an der Universität Wien. II. Teil. Beschreibung ausgeführter Anlagen usw. Mit 52 Abbildungen im Text. Monographien über angewandte Elektrochemie. Herausgegeben von VIKTOR ENGELHARDT. XLIII. Band. Halle a. S.: Verlag von Wilhelm Knapp. 1913. pp. viii + 182. Price, M. 9.60.

In Part I of the electrolytic decomposition of alkali chlorides[1] the author reviewed the leading American, British and German patents; in Part II he aims to give descriptions of the principal plants. They are classified according to the arrangement of diaphragms and anodes under two heads; one head has two, the other, three subdivisions. Each division receives a brief discussion.

Of the 169 pages dealing with the plants proper, the Griesheim-Electron process receives 97 pages. It is treated by B. Scheid who has had considerable practical experience in a Griesheim plant. This is quickly recognized in the treatment of the subject, which is replete with the practical details that ought to be found in a monograph, but rarely are, as few electrochemical subjects are discussed by the men in the works. This part of the treatise alone would make the book valuable to the chemical engineer. The rest of the book, discussing the four remaining general methods of operating, resemble the usual discussions of electrochemical subjects; they are general in character, as details are not permitted to appear in print.

H. O. HOFMAN

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[1] THIS JOURNAL, **49**, 74 (1913).

THE PLANT ALKALOIDS. By THOMAS ANDERSON HENRY, D.Sc. (LOND.), F.C.S., Superintendent of Laboratories, Scientific and Technical Department, Imperial Institute. Philadelphia: P. Blakiston's Son & Co. 1913. pp. vii + 466. Price, $5.00.

In view of the increasing attention which is being continually directed to the field of alkaloidal chemistry, any new book on the subject awakens interest. Particularly is this true in the light of the advances that have been made in synthetic and constitutional studies since the first synthesis of conine by Ladenburg in 1886.

In his book on "The Plant Alkaloids," Dr. Henry has followed in general the example of Pictet and others in adopting a classification in accordance with the nature of the simpler bases from which the alkaloids may be derived and in conjunction therewith a subclassification depending on the natural source of the alkaloids.

The scope of the work includes a consideration of the preparation, estimation, general properties, constitution and physiological action of the alkaloids.

In the treatment of the constitution of the alkaloids, the discussion is not as clear and discriminating as that presented by Winterstein and Trier in "Die Alkaloide" (1910), or as that found in the earlier work of Pictet on "The Vegetable Alkaloids."[1] Nor is the presentation of the results of some of the more recent researches as full as might be desired. The value of the work would be considerably enhanced if the author had included a fuller consideration of qualitative tests for the alkaloids and had, in conjunction with their physiological properties, presented some of the common antidotes.

The work, however, is as a whole comprehensive in its development and is consequently well adapted to general usefulness. The sections on the preparation and estimation of some of the more important alkaloids add very considerably to the practical value of the work. The book, indeed, merits the appreciative consideration of the chemical public.

H. C. BIDDLE

DAS LEBENSMITTELGEWERBE. Ein Handbuch für Nahrungsmittelschemiker, Vertreter von Gewerbe und Handel, Apotheker, Arezte, Tierärzte, Verwaltungsbeamte und Richter. Herausgegeben von. Prof. Dr. K. VON BUCHKA, Geheimer Ober-Regierungsrat und Vorstand der Kaiserlichen Technischen Prüfungsstelle in Berlin. Mit zahlreichen Tafeln und Abbildungen. Band I, 1. Lieferung. Die Menschliche Nahrung, von DR. A. KREUTZ, Professor an der Universität Strassburg in E. Leipzig: Akademische Verlagsgesellschaft m. b. H. 1913. pp. 48. Price, M. 2.00.

In this new manual is discussed a consideration of the foodstuffs as they occur in natural products, alcoholic beverages, spices and food accessories and the adulterations commonly practiced. Up to the present a single chapter has appeared, dealing with the foodstuffs. The treatment given the subject follows closely the usual text-book description and affords nothing unusual. FRANK P. UNDERHILL

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[1] English edition, 1904, John Wiley & Sons.

AN INTRODUCTION TO THE PHYSICS AND CHEMISTRY OF COLLOIDS. By EMIL HATSCHEK. Reprinted from the Chemical World. Text-Books of Chemical Research and Engineering. Philadelphia: P. Blakiston's Son & Co. pp. ix + 94. Price, $1.

This book is "based on a course of ten lectures delivered to students of varied attainments and interested in every branch of chemistry and chemical industry" and is a clear, concise and inclusive discussion of the main facts and theories of colloid chemistry, with references to specific colloids only in illustration of general principles. It would serve as an excellent résumé of the subject for any one wishing to be intelligently informed with a minimum expenditure of time. On p. 34 the statement that barium sulphate has never been prepared in the colloidal state should at least be qualified, as von Weimarn has prepared it from alcohol solutions, and that on p. 77 that one trivalent ion carries the same charge as two divalent ions is evidently a slip. H. I. MATTILL

REVIEW QUESTIONS AND PROBLEMS IN CHEMISTRY. Compiled by M. S. H. UNGER, A.M., Headmaster of St. Johns School, Manlius, New York. Boston, New York, Chicago, London: Ginn & Co. pp. v + 106. Price, 50 cents.

The book consists of a number of questions and problems "taken from the most recent college, College Board, and Regents of the State of New York examinations, and from the latest and most authoritative text-books, and will be found from the author's experience more than sufficient to prepare a student for the entrance examinations for any college, or for the College Board examinations."

The above words from the preface give an adequate idea of the nature of this little book. C. A. R.

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FRACTIONATION OF CALIFORNIA PETROLEUM BY DIFFUSION THROUGH FULLER'S EARTH[1]

By J. Elliott Gilpin and P. Schneeberger

For several years investigations have been in progress in this laboratory upon the effect produced by diffusion of petroleum oils through fuller's earth. These investigations were pursued in order to obtain some idea of the changes produced in the process of diffusion to which the oils have been subjected in their passage from the place of formation to their present location; also, to gain some idea of the substances present in the natural oil by a separation of the constituents by a process not involving the use of heat, and thereby producing changes by cracking and otherwise. The results obtained when a light oil from Pennsylvania and a heavier oil from Illinois were thus fractionated have already been published.[2] In the present investigation, this method of fractionation was extended to a very heavy petroleum from California. As will be later described, the different fractions obtained by such diffusion were studied with regard to their content of paraffin, benzene, and olefin hydrocarbons, and to the amount of sulphur and nitrogen compounds found in them and in the earth through which they passed. For the sake of comparison, the behavior of mixtures of known amounts of benzene and pure paraffin oil, when allowed to diffuse through fuller's earth, were also studied.

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[1] This research was aided by a grant received from the C. M. Warren Committee of the American Academy of Arts and Sciences.

[2] Gilpin and Cram: "The Fractionation of Crude Petroleum by Capillary Diffusion," This Journal, **40**, No. 6, December, 1908. Gilpin and Bransky: "The Diffusion of Crude Petroleum through Fuller's Earth," *Ibid.*, **44**, No. 3, September, 1910.

DESCRIPTION OF OILS USED

California Oil I.—Viscous, brownish black in color; of a syrupy consistency, and failed to flow from a small vessel when cooled to —10°; possessed a disagreeable odor, suggestive of organic sulphur compounds; specific gravity at 20°, 0.912; when distilled, the first fraction came over at 90°, colorless and agreeable in odor; the last fraction came at 380°, brown, disagreeable in odor, resembling garlic, but supposed to be due to hydrides of the hydrocarbons, formed during the cracking of the oil; analysis showed appreciable amounts of sulphur compounds present. This oil came from Kern County, California.

California Oil II.—Less viscous than the first oil, and of less disagreeable odor; specific gravity, taken with a delicate Westphal balance at 20°, 0.8890; when distilled, fractions were obtained from 100° to 350°; contained a small proportion of benzene hydrocarbons and 0.760 per cent. of nitrogen compounds; no trace of sulphur compounds was found. The oil came from Well No. 1, Section 30–30–24, Elk Hills, Kern County.

California Oil III.—Fairly viscous, brownish black oil, of somewhat disagreeable, smoky odor; specific gravity, 0.9118 at 20°; when distilled, fractions were obtained from 105° to 340°, attempts to obtain fractions at higher temperatures resulting in the cracking of the oil, giving fractions ranging around 270°; rich in benzene and olefin hydrocarbons, but entirely free from nitrogen and sulphur compounds; its properties resembled closely those of the first California oil. The petroleum came from Well No. 1, Section 30, Elk Hills, Kern County.

Pennsylvania Oil.—A light, thin, dark brown oil from Venango County, Pennsylvania; possessed an agreeable odor; specific gravity at 20°, 0.8470. This was the same oil that had been investigated by Gilpin and Cram, and Gilpin and Bransky. Between the time when this oil was first studied and its investigation in 1912 and 1913, its specific gravity had increased from 0.810 to 0.8470 by evaporation through the barrel staves.

INVESTIGATION OF CALIFORNIA OIL I

The oil first studied was the heavy petroleum from Kern County, California. A description of this oil, named the California Oil I, is found on page 60.

The method of handling this oil was practically the same as that introduced by Gilpin and Cram and improved by Gilpin and Bransky. The apparatus in which the diffusion was carried out was similar to that employed by Gilpin and Bransky. Two minor additions were made to the apparatus. The first of these was a manometer which recorded pressures from 730 mm. to 0 mm. when attached to the exhaust system. The other was a device which it was found necessary to put in series with the exhaust system, owing to the fact that the exhaust was obtained by use of a large Chapman water pump. Fluctuations in the water pressure were accompanied by fluctuations in the amount of exhaust. The device by which the suction could be maintained uniform for any length of time consisted of a sliding tube with perforations at its lower end, that could be adjusted by raising or lowering in a reservoir of mercury according as lower or higher pressures were desired.

It was found at the start that an oil as heavy as this one could not be made to diffuse of itself by capillarity at room temperatures (19° to 23°). To produce the necessary diffusion, reduced pressures were brought to bear, pressures as low as 12 mm. of mercury being maintained for days at a time.

In the preliminary experiments, sixteen tubes were filled with fuller's earth.[1] The tubes were filled by dropping into them an amount of earth that would form a column about a foot in height. Since all ranges of compactness of the earth were desired, the earth in some tubes was not compressed in any way. In others it was rammed slightly by a rod tipped with a rubber stopper. In a third set, it was rammed fairly hard, and in a fourth as hard as possible. The tubes were then allowed to stand undisturbed for a short while, so as to permit the cushions of air held between layers of the earth to escape. A second column of earth a foot in height was then added, the same degree of packing observed, and the process repeated until the tubes were filled. They were then placed with their lower ends in separate reservoirs of oil, and a reduced pressure of 600 mm. was then applied to the upper ends. This failed to produce any diffusion, as could be determined by the level of the oil in the reservoirs, so the pressure was gradually reduced until 20 millimeters of mercury were registered on the manometer. There was, however, no sign of actual fractionation of the oil in any of the tubes, but, instead, at the low pressure that was employed the oil was drawn up through the earth unchanged in any of its properties.

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[1] This earth, known as "XXF Clay," and the fuller's earth used in later work were obtained by courtesy of the Atlantic Refining Co., Philadelphia, Pa.

An explanation of the failure of the oil to fractionate was found in the high viscosity of the petroleum. The oil, instead of diffusing through each minute particle of earth, was sucked around the particles and emerged unaltered at the top of the tube.

The cause of the high viscosity of the oil was doubtless the very large quantity of bitumen and the complex hydrocarbons present, whose boiling points were as high as 380°. Accordingly, efforts were directed toward reducing the viscosity of the oil by coagulating the bitumen. It was shaken with a solid electrolyte and with a solution of the same, but repeated experiments failed to show any perceptible reduction in specific gravity or viscosity, nor was there any noticeable coagulation of the bituminous material held in suspension in the oil.

It was observed, however, that any rise in temperature of the oil was accompanied by a marked decrease in viscosity. Accordingly, the effect of this reduction in viscosity upon the fractionation of the crude petroleum was next studied. In order to secure uniform conditions, it was deemed advisable to have the reservoirs for the oil and also the lower part of the tubes immersed in a large water bath, the temperature of which could be regulated and maintained uniform by a gas thermostat. An appliance that could withstand the action of the heated water and oil was, therefore, devised. Glass bottles, fitted with water-tight stoppers and safety tubes, could not be employed, for these broke when temperatures above 60° were reached. For the fractionation at high temperatures, each tube was constructed of brass, and was made to fit snugly into a closed reservoir of a liter in volume. Contact between the tube and the neck of the reservoir was made perfect by having a lead washer which was held rigidly between the two by a nut that screwed down upon the neck of the reservoir.

To determine the most desirable temperature at which the experiments should be carried out, the viscosity of the oil was measured at different temperatures. The apparatus was the same as used by a previous experimenter.[1] With the viscosimeter it was found that a measured quantity of the oil used by Bransky diffused at the following rates:

4.5 cc. of Pennsylvania Oil (sp. gr. 0.8470):

	Minutes
At 20°	10.25
At 40°	6.00

When a similar quantity of the California Oil I was run through the viscosimeter, it was found that the time required was vastly greater. The following results were obtained at different temperatures:

Table I

4.5 cc. California Oil I (sp. gr. 0.912)

	Minutes
At 20°	84.0
At 40°	41.0
At 60°	17.5
At 75°	11.3
At 90°	8.1

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[1] This Journal, **44**, No. 3.

From the above results, it is apparent that a temperature of at least 75° is necessary for diffusion, since the viscosity of the oil at lower temperatures was so great as to prevent its fractionation by diffusion. The temperature of 90° was ruled out because at that temperature there was a tendency for the lightest ingredients of the oil to distil off. This was determined by keeping a measured quantity of the oil at 90° for a week. A quantity amounting to about two per cent. was found to distil off. For this reason it was deemed advisable to carry on the diffusion of the oil at 75°.

Accordingly, eight tubes packed with varying degrees of hardness were maintained at 75°, and at the end of nine days these yielded the first fractions of the heavy California oil (specific gravity, 0.912). Nearly 90 liters of the oil had to be used to obtain the four fractions in the amounts shown below:

Table II—First Fractionation of California Oil I

Fraction	Sp. gr.	Quantity Liters
1–A	0.8695[1]	1.2
1–B	0.882	1.4
1–C	0.9025	1.8
1–D	0.904	1.75
	Total	6.15

There was thus secured a small proportion of available fractions. This was obtained, however, only after very great difficulties had been overcome and with a loss of nearly 93 per cent. of the original oil. The results demonstrate, nevertheless, the possibility of fractionating a heavy, viscous petroleum. Owing to the difficulties encountered in working with large quantities of the oil at elevated temperatures, it was decided to discontinue work on this heavy petroleum until more adequate means of handling it under the necessary conditions were at the disposal of the experimenter.

The four fractions from the California Oil I, designated as 1–A, 1–B, 1–C and 1–D, were then analyzed for their sulphur content. Similar determinations were made for the oil retained by the earth.

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[1] All specific-gravity measurements were taken at exactly 20° with a delicate Westphal balance.

Determination of Sulphur Compounds in the California Oil I

The odor of the high-boiling fractions of this oil led to the suspicion that sulphur compounds were present. Accordingly, qualitative tests were made to detect the presence of this element. These tests were as follows:

About 10 cc. of the sample to be tested were heated to boiling in a flask provided with a reflux condenser. About half a gram of metallic sodium was introduced, and the liquid heated to the boiling point for about thirty minutes. After cooling to room temperature, water was gradually introduced through the condenser and the flask shaken until the sodium had gone into solution. The solution of the hydroxide containing the sodium sulphide was separated, and the addition of sodium nitroprusside produced a purplish blue or deep purple coloration. A quicker method for the qualitative determination of sulphur was one that is employed in the petroleum industry. A solution of litharge in concentrated potassium hydroxide solution was prepared. The undissolved litharge was allowed to settle, and the clear solution decanted. Several cc. of the oil to be tested were shaken with a small quantity of the potassium plumbite solution, and the oil allowed to rise. The plumbite solution was colored from pale brown to black, according to the amount of sulphur present.

Quantitative determination of sulphur by the usual Carius method failed, the bombs exploding in every one of the fifteen analyses that were attempted. Carius determinations made in hard glass tubes gave no better results. A modified Carius method was then employed. This was essentially as follows: A weighed sample of the oil was introduced into a Carius tube and 5 cc. of fuming nitric acid were poured upon it. The open tube was then heated for two hours in a water bath at 100°. Five more cc. of the acid were then added, and the heating repeated for two more hours. Then five cc. of the acid were again introduced, the tube was drawn out and sealed, and then heated for two hours in a bomb furnace at 280°. The charge of the tube, when cool, was emptied into several hundred cc. of water, and the sulphur determined as barium sulphate by the usual method. This modified Carius method gave results that were somewhat lower than the results obtained by the methods finally employed. This was probably due to the volatilization of the sulphur compounds when the open tube was heated.

The methods found to be most satisfactory, however, were the Sauer combustion method, described in detail in Morse's Exercises in Quantitative Chemistry (pp. 258–60), and a method by which the oil was oxidized in a flask by concentrated nitric acid and potassium chlorate. The two methods gave concordant results. In every instance duplicate analyses were made, and the mean result given in the table below. The fractions analyzed were those described on p. 64.

Table III—Analysis for Sulphur

Fraction	Sp. gr.	Per cent. sulphur
1–A	0.8695	0.11
1–B	0.882	0.144
1–C	0.9025	0.174
1–D	0.904	0.29
Crude oil	0.912	0.541

In order to see if the proportion of sulphur could be further reduced by filtration through fuller's earth, Fractions A and B were refractionated and the results of the second fractionation were analyzed with respect to their sulphur content. The fractions from A are designated as 1–A 1, 1–A 2 and 1–A 3; those from 1–B as 1–B 1, 1–B 2 and 1–B 3.

Table IV—Second Fractionation: Analysis for Sulphur

Fraction	Sp. gr.	Per cent. sulphur
1–A 1	0.857	0.06
1–A 2	0.8604	0.07
1–A 3	0.869	0.104
1–B 1	0.8625	0.072
1–B 2	0.8771	0.09
1–B 3	0.8803	0.141

The results tabulated above show that there is a gradual absorption of sulphur compounds by the fuller's earth. Those fractions that collect at the top of the tubes have the smallest proportion of the sulphur compounds in them, and the amount increases as fractions lower down are taken. The explanation of the comparatively small amount of sulphur in the uppermost fraction is probably as follows: the original petroleum penetrates a grain of the porous fuller's earth, emerges on the other side and has a portion of its sulphur removed and retained by the earth. The possible mechanism of this selective absorption by the earth is discussed later. The oil then enters another grain of earth, the absorptive action of the earth is repeated, and more of the sulphur is removed. The oil that thus penetrates by diffusion up to the top of the tube has passed through the greatest number of grains of earth and thus contains less sulphur than the oil that has not penetrated so far. Moreover, the oil that follows in the track of the first particle of oil which penetrates the earth finds particles of earth that have already taken up the greatest quantity of sulphur that is possible for them to absorb. Hence the second particle of oil passes through earth that is already saturated with respect to its power to absorb sulphur compounds, and it may pass through unchanged, or nearly so. This accounts for the fact that the fractions that are nearest to the original petroleum have chemical and physical properties that closely resemble those of the crude petroleum.

Judging from the results obtained from the second fractionation, it is probable that if enough of the lighter fractions were available for carrying on several more fractionations, the sulphur could be entirely removed.

In order to show to what extent the earth retained the sulphur compounds which were originally in the oil, the earth from which the oil had been displaced by the addition of water was extracted with ether. By this process, oils were obtained which were heavier than those oils expelled by the addition of water. These were analyzed for sulphur, with the following results:

Table V—Analysis of Oil Retained by Earth

Section of earth	Sp. gr.	Per cent. sulphur
Oil extracted from A	0.8955	0.11
Oil extracted from B	0.9038	0.237
Oil extracted from C	0.9105	0.42
Oil extracted from D	0.927	0.675

These results show that it is undoubtedly the earth through which the oils pass that retains the sulphur compounds. They show, moreover, that the earth in the lowest parts of the tube absorbs so much of the sulphur compounds from the oil that passes through them that the proportion of these compounds in the lower end of the tube indicates a concentration that is greater than that in the original petroleum.

INVESTIGATION OF CALIFORNIA OIL II

In working with the heavy California petroleum from which the fractions described above were obtained by diffusion at elevated temperatures, it was pointed out that such fractionation was exceedingly difficult to effect, and at an enormous loss of petroleum. Owing to these results a lighter oil from the same locality was secured. This lighter oil was the one described as the California Oil II (see p. 60). Its properties were somewhat different from the oil first studied. The principal physical differences noted were viscosity and specific gravity, the latter being 0.889 in contrast to 0.912, that of the California Oil I. The viscosity was taken at various temperatures with the following results:

Table VI—Viscosity Measurements of California Oil II (4.5 cc. Run Through)

Temperature of oil	Time Minutes
20°	24.0
30°	17.1
40°	12.2
50°	9.1

It was decided to work with this oil at room temperature, owing to the difficulties arising from the fractionation of large quantities of oil at elevated temperatures. Attention was then turned toward the problem of finding the length of tube most desirable for fractionating an oil of specific gravity 0.889 at 20°.

It was necessary, in addition, to ascertain the proper amount of pressure that should be brought to bear to bring about diffusion. For this purpose glass tubes of 3.2 cm. in diameter and varying in length from 30 to 150 cm. were employed. The object in using glass tubes was to enable the observer to see to what extent fractionation was taking place as the amount of pressure on the tubes was changed. It was soon found that a fractionation of the petroleum could be produced working at room temperatures. While the results obtained were not as satisfactory as those obtained with light Pennsylvania oil of specific gravity 0.8470, they demonstrated the possibility of fractionating an oil of specific gravity 0.889 by diffusion through fuller's earth at ordinary temperatures. The yield of available fractions, however, amounted to only twenty per cent. of the oil used, while in the case of the lighter Pennsylvania oil, it was 45 to 50 per cent. of the petroleum used.

The length of tube that gave the most satisfactory results was found to be about 90 cm. The degree of compactness of the earth that gave best results was obtained by tapping the sides of the tube, and refraining from ramming, as all previous packing had been done. A column of earth a foot long was introduced into the tube, and it was tapped lightly on its side until the top of the column presented a firm surface.

The method employed in extracting the oil from the earth into which it diffused consisted in taking measured sections from the earth[1] after it had been carefully emptied into a cylinder that was split longitudinally, and adding water to each section. The water formed a thick emulsion with the earth and expelled a part of the oil, retaining, however, an oil that was heavier than that expelled. It was noticed that the lighter oils were displaced in much greater proportion than were the heavier oils, for the earth showed a tendency to remain in mechanical combination with the oil, holding almost

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[1] The section of earth from the uppermost part of the tube was called A, and the oil extracted therefrom called 2–A. The next lower section was called B, and its oil 2–B, etc.

100 per cent. if the specific gravity approached 0.9. When an examination of the oil retained by the earth was desired, the oil was extracted from the dried earth by ether. By the ether extraction an oil of different physical and chemical properties was secured. This proved that the fractions obtained by displacement of the oil by water did not represent the actual fractions formed during diffusion through the earth, but only a small part of such fractions.

The method of securing fractions of oil by displacement by water was then dispensed with and another method introduced. This consisted in allowing the oil to diffuse to the top of the tube and then letting it overflow into small tubes of about 70 cc. capacity. The oil that first overflowed and collected in the upper reservoir constituted the first fraction. The first fraction was usually very light in color and specific gravity. As the diminished pressure continued to be applied, a heavier oil began to flow into the upper reservoir. When a change in color was noticeable, the reservoir was emptied or exchanged for another, and the pressure was temporarily cut off from the tube by means of pinchcocks while the change was being made. The second fraction was then collected until a change in color was noticed, and so on with a third, until an oil that was colored brown by the bitumen of the petroleum drained into the upper reservoir. The reduced pressure was then cut off, the tubes cleaned and refilled with fresh fuller's earth, and the process repeated.

By repeated experiment, the amount of pressure that gave the best results was determined and regulated as follows: the tubes were allowed to stand in the reservoirs of petroleum for abour 24 hours, without any reduced pressure being applied. Then, for a period of about three days, the pressure was gradually reduced until the manometer registered 650 mm. of mercury. After being maintained at this height for several days, the pressure was then lowered to 500 mm. and kept there until the first fractions overflowed into the upper reservoirs. When this pressure failed to draw up a slow, steady stream of oil into the reservoirs, it was still further reduced, usually being made as low as 200 mm., by the time that the last available fraction had been collected.

By this method of operating, the California Oil II was found to be capable of fractionation into five distinct fractions. The lightest, termed Fraction 2–A, was of specific gravity 0.8264; the heaviest, 2–E, 0.8737, showing a wide range in density (see p. 72).

The basis upon which the various fractions were differentiated was their color, as it was observed that the depth of color was an approximate measure of the specific gravity of the oil.

The fractions 2–A to 2–E were examined for nitrogen, and all of them showed signs of its presence. Careful analyses of these were then made, and similar analyses of the earth in various parts of the tube were made. Fractions 2–A and 2–B were then subjected to a second fractionation, and the results also studied with regard to their nitrogen content.

Determination of Nitrogen Compounds in California Oil II

Nitrogen compounds were found to exist in the California Petroleum II to the extent of nearly 0.8 per cent. Accordingly, this oil was subjected to fractionation by the improved method that was adopted by the investigator (see p. 70). This was necessary since the oil was too heavy to be worked by the method of Cram and Bransky unless elevated temperatures were resorted to in order to reduce the viscosity. Besides, it was feared that high temperatures would bring about the loss of the nitrogen compounds by volatilization.

The method for determining the nitrogen was that known as the Gunning-Arnold-Dyer modification of the Kjeldahl method. It is described in detail in Sherman's Organic Analysis (pp. 291–4). It was found necessary to digest the light oils as long as 3 or 4 hours and the heavy ones as long as 8 hours before the contents of the digestion flask became colorless. Another necessary precaution had to be observed in applying heat very gradually to the flask at the beginning of the digestion, otherwise the nitrogenous material distilled off, giving results that were far below those obtained when greater precaution was exercised.

Table VII— Nitrogen Determinations

Fraction	Sp. gr.	Per cent. nitrogen
2–A	0.8264	0.08
2–B	0.8421	0.116
2–C	0.852	0.289
2–D	0.8614	0.315
2–E	0.8737	0.332
Crude oil	0.889	0.761

These results show that the proportion of nitrogen compounds is reduced in the lightest fraction to nearly one per cent. of its total amount. This proportion of nitrogen was still further reduced by the second fractionation of the two lightest fractions. The fractions obtained from 2–A are designated by 2–A 1, 2–A 2, etc. Those from 2–B are designated by 2–B 1, 2–B 2, etc.

Table VIII—Second Fractionation of California Oil II

Fraction	Sp. gr.	Per cent. nitrogen
2–A 1	0.8117	Trace
2–A 2	0.8186	Trace
2–A 3	0.8193	0.03
2–A 4	0.8240	0.06
2–B 1	0.8205	Trace
2–B 2	0.8386	0.045
2–B 3	0.8414	0.09
2–B 4	0.8421	0.109

From the above results it is apparent that the fuller's earth is particularly potent in selectively absorbing nitrogen compounds from the oil. In view of the fact that but two filtrations through the earth succeeded in reducing the amount of nitrogen present to such a small proportion as compared to that in the petroleum, it is probable that a third filtration would have reduced it to zero. A third fractionation would have been made, but lack of workable material rendered this impossible.

The analysis of the oil retained by the earth taken from the upper, middle and lower ends of the tubes showed that the part in the lowest sections of the tube had absorbed the greatest amount of the nitrogen compounds from the petroleum. The oil was extracted from sections of earth, taken at different levels from the tubes, by ether. The ether was evaporated off in an electrical drying oven at 50°.

Table IX—Analysis of Oil Retained by Fuller's Earth

Section of tube	Sp. gr.	Per cent. nitrogen
Upper end	0.8413	0.205
Middle section	0.8655	0.43
Lower end	0.9172	0.94

The concentration of the nitrogen compounds in the lower end of the tubes is apparent. It is noticeable that the percentage of nitrogen here is slightly greater than it was in the original petroleum. This was to be expected, inasmuch as the earth in the lower end of the tube came into contact with the greatest amount of oil and could thus selectively absorb more of the nitrogen compounds than earth in the upper end. Moreover, earth in the upper end came into contact with oil that had already had a portion of its nitrogen compounds removed and could not, for that reason, extract as much nitrogenous material from it as it could from oil that was much richer in nitrogen compounds.

The study of the benzene and olefin hydrocarbons in California petroleum was next contemplated. Before taking this up, it was considered advisable to study with some degree of accuracy the behavior of known mixtures of benzene and pure paraffin oil where such mixtures were allowed to diffuse through fuller's earth. This problem had been investigated before by earlier workers in this field, and certain conclusions arrived at, but a further study of the same, working under somewhat different conditions, was now resumed.

FRACTIONATION OF MIXTURES OF BENZENE AND PARAFFIN OIL

In previous work by Gilpin, Cram and Bransky on the fractionation of crude petroleum, it was noted that there was a tendency for the pure paraffin hydrocarbons to collect in the upper section of the tube through which the petroleum was allowed to diffuse. To investigate this more closely, Gilpin and Bransky studied the behavior of mixtures of benzene and paraffin oil, such mixtures being of definitely known composition, and plotted their results in curves that showed the relative amounts of benzene and paraffin oil that collected in all parts of the tube. The curves show, moreover, that the proportion of benzene decreases gradually as one passes from Grade F (the oil from the lowest section of the tubes) to Grade C (the oil from the third section of the tubes), Grade A being considered that fraction from the uppermost part of the tubes. Above Grade C, there is a sharp decrease in the proportion of benzene, the same dropping far below the proportion in the original mixture that was put into the reservoir. It was also noted that the curves representing the specific gravities of the various sections were about parallel with those representing the percentages of benzene. This was to be expected, since the benzene was of considerably higher specific gravity than the paraffin oil. The tubes employed measured five feet six inches in length.

With the view to determine more accurately the exact location of the break in the curve, and to ascertain if it was a function of the length of the tube, investigation along this line was begun by the authors. In order to study the latter problem, it was decided to use shorter tubes, those of two feet nine inches in length being chosen. Correspondingly smaller sections of earth were taken, and the oil was displaced from them by the addition of water.

The benzene used was of specific gravity 0.879. The method of analysis used to determine the proportion of benzene and paraffin oil in each fraction consisted in shaking 10 cc. of the oil with three or four times its volume of concentrated sulphuric acid, until all of the benzene had been sulphonated. Then the shaken material was poured into a burette and allowed to stand until all the paraffin oil mechanically held in combination with the acid had separated out.

To determine the length of time necessary for shaking in order to remove all the benzene, 10 cc. of benzene were mixed with an equal quantity of pure paraffin oil and the mixture shaken with four times its volume of concentrated sulphuric acid in a machine that agitated the mixture about 450 times per minute. The amounts of benzene that were absorbed after definite periods of time were as follows:

Table X —Action of Sulphuric Acid on Benzene and Paraffin Oil

Time of shaking Minutes	Per cent. benzene absorbed
15	52.1
30	79.0
45	91.4
60	100.0

All samples for analysis were, therefore, shaken for more than an hour, until further shaking failed to reduce the volume of the oil.

The paraffin oil used was a light, pale yellow oil of very disagreeable odor. Its specific gravity was 0.7895 at 20°. After purification by the method described below, the specific gravity became 0.7775. The oil was purified as follows: A quantity was agitated with one-third its volume of concentrated sulphuric acid for 6 hours in two 2-liter bottles that revolved slowly about an axis placed between the two. The acid became dark brown, and the evolution of sulphur dioxide indicated chemical action. The acid was then drawn off in a large separatory funnel and a fresh supply added to the oil. This was again agitated for six hours and separated off as before. By this process the volume of oil decreased 9.3 per cent., and lost its disagreeable odor and became colorless. It was then shaken with a small quantity of dilute alkali until neutral, washed with water, and finally shaken for several hours with calcium chloride, and filtered. By repeated tests it was shown that the oil, after this treatment, did not decrease in volume when shaken with sulphuric acid.

Mixtures of benzene and pure paraffin oil were then allowed to diffuse through fuller's earth. The earth in the tubes had been as tightly packed as it was possible to secure by ramming the earth with a rod tipped with a rubber stopper. The proportions of benzene and paraffin oil in the mixtures were as follows:

Name applied to mixture	Per cent. benzene	Per cent. paraffin oil
Series No. 5	20	80
Series No. 6	33	67
Series No. 7	50	50
Series No. 8	75	25
Series No. 9	20	80
Series No. 10	33	67
Series No. 11	50	50
Series No. 12	20	80
Series No. 13	75	25
Series No. 14	20	80

Sections of varying lengths, as shown in the tables accompanying the curves (pp. 77 to 83), were taken, and the oil was displaced by addition of water (in Series No. 5 to No. 8, inclusive), by extraction with ether (Series No. 9), or by letting the oil overflow into upper reservoirs by the new method described on page 70 (Series No. 14).

The sections of earth from which the oil was extracted were made considerably smaller than similar sections taken by Bransky in his work. The uppermost section, called A, varied in length from 25 to 12 cm. The fraction of oil that it yielded was called 5–A, 6–A, according to the series to which it belonged. The next lower section of earth, usually a little shorter than A, was called B. Its oil was termed 5–B, 6–B, or 7–B, according to the series to which it belonged. The short tube and short sections of earth from which the oil was extracted were chosen so as to locate more accurately the point at which a sharp decrease in the amount of benzene occurred. This point of sudden change was found to be invariably located from 20 to 40 cm. from the top. The specific gravity of each fraction of the oil was taken for the first five tubes. Since this in every case was a function of the proportion of benzene and paraffin oil present, it was discontinued after the first five series were run.

Series No. 5 consisted of the following: A tube was filled with earth and the reservoir below filled with 500 cc. of a mixture of 20 per cent. of benzene of specific gravity 0.879 and 80 per cent. of paraffin oil of specific gravity 0.7775. When diffusion had taken place, the fractions were analyzed as before described, and it was found that the break in the curve occurred at about 35 cm. from the top. The specific gravity of that fraction that contained least benzene was the lowest. It was noticeable that the proportion of benzene to paraffin oil was nearly a constant, until the point B was reached (see Fig. I).

Table XI—Series No. 5

Benzene, 20 per cent. Paraffin Oil, 80 per cent.
Rose to a height of 88 cm.

Fraction	Cm.	Cc.	Sp. gr.	Per cent. benzene	Per cent. paraffin
5–A	20	46	0.787	10.4	89.6
5–B	15	44	0.790	19.1	80.9
5–C	15	43	0.791	21.3	78.7
5–D	15	36	0.792	21.0	79.0
5–E	12	30	0.792	21.3	78.7
5–F	11	39	0.795	23.3	76.7

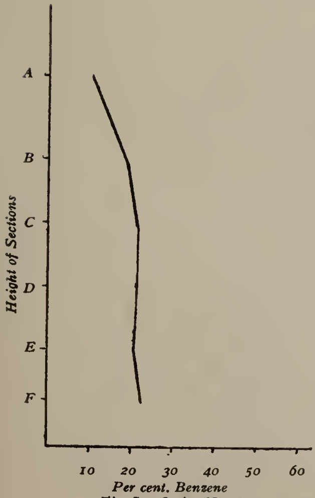

Fig. I.—Series No. 5

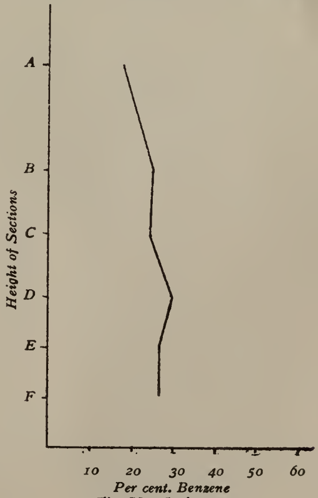

Fig. II.—Series No. 6

In Series No. 6 there was not noticed as marked uniformity in specific gravity or in the proportion of benzene to paraffin oil as in Series No. 5. The break in the curve occurred about 25 cm. from the top (see Fig. II).

Table XII—Series No. 6

Benzene, 33 per cent. Paraffin Oil, 67 per cent.
Rose to a height of 95 cm.

Fractions	Cm.	Cc.	Sp. gr.	Per cent. benzene	Per cent. paraffin
6–A	25	31	0.725	18.4	81.6
6–B	15	38	0.798	25.7	74.3
6–C	15	42	0.798	25.3	74.7
6–D	12	38	0.799	25.9	74.1
6–E	12	35	0.7995	27.3	72.7
6–F	12	45	0.799	27.0	73.0

Series No. 7, with equal quantities of benzene and paraffin oil, gave a curve that broke sharply at Section B, 16 cm. from the top. Up to this point the amounts of the two oils remained nearly constant (see Fig. III).

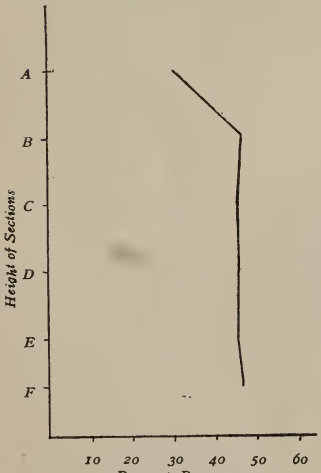

Fig. III.—Series No. 7

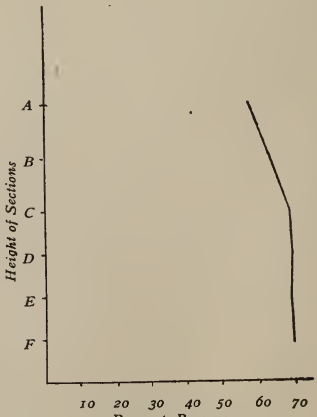

Fig. IV.—Series No. 8

Table XIII—Series No. 7

Benzene, 50 per cent. Paraffin Oil, 50 per cent.
Rose to a height of 90 cm.

Fractions	Cm.	Cc.	Sp. gr.	Per cent. benzene	Per cent. paraffin
7–A	16	21	0.8023	30.5	69.5
7–B	16	34	0.8155	47.0	53.0
7–C	16	44	0.8160	45.8	54.2
7–D	16	50	0.8165	45.7	54.3
7–E	12	48	0.8165	45.7	54.3
7–F	12	53	0.817	47.2	52.8

In Series No. 8 the break was not such a sharp one, and occurred about 30 cm. from the top (see Fig. IV).

Table XIV—Series No. 8

Benzene, 75 per cent. Paraffin Oil, 25 per cent.
Rose to a height of 84 cm.

Fractions	Cm.	Cc.	Sp. gr.	Per cent. benzene	Per cent. paraffin
8–A	15	25	0.832	58.1	31.9
8–B	15	37	0.833	64.5	35.5
8–C	12	38	0.8385	69.0	31.0
8–D	12	44	0.839	69.8	30.2
8–E	12	43	0.839	69.7	30.3
8–F	12	51	0.842	70.1	29.9

In order to determine whether the proportion of benzene to paraffin oil in the fractions was affected by the displacement of the oil by water, the fractions secured from Series No. 9 were extracted with ether. The results plotted in the curve on page 80 show that the water plays no part whatever in the action. The break in the curve, showing a sudden sharp decrease in the proportion of benzene to paraffin oil, occurred in about the same locality.

Table XV—Series No. 9

Benzene, 20 per cent. Paraffin Oil, 80 per cent.
Rose to a height of 70 cm.

Fractions	Cm.	Cc.	Per cent. benzene	Per cent. paraffin
9–A	12	44	8.9	91.1
9–B	12	34	18.4	81.6
9–C	12	38	20.0	80.0
9–D	10	37	21.7	79.3
9–E	10	39	21.3	79.3
9–F	10	44	22.1	78.9

In Series No. 10 and No. 11 (Figs. VI and VII) the individual fractions were analyzed immediately after the displacement of the oil in the earth by water. This was done so as to avoid any possible loss of either oil by evaporation. The same general characteristics are apparent in the curves that express the results of the fractionation.

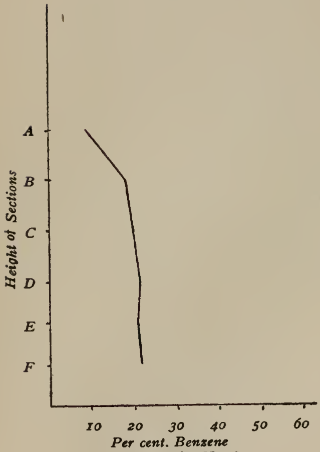

Fig. V.—Series No. 9

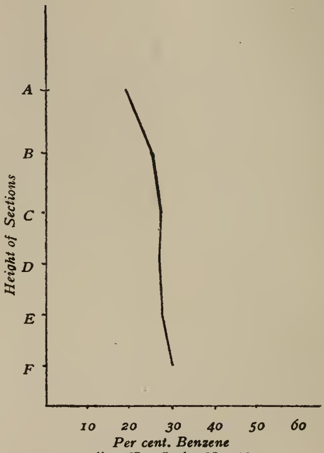

Fig. VI.—Series No. 10

Table XVI—Series No. 10

Benzene, 33 per cent. Paraffin Oil, 67 per cent.

Rose to a height of 81 cm.

Fractions	Cm.	Cc.	Per cent. benzene	Per cent. paraffin
10–A	15	36	20.1	79.9
10–B	15	53	26.2	73.68
10–C	12	45	28.0	72.0
10–D	12	52	27.7	72.3
10–E	12	42	28.1	71.9
10–F	10	37	30.4	69.6

Table XVII—Series No. 11

Benzene, 50 per cent. Paraffin Oil, 50 per cent.
Rose to a height of 74 cm.

Fractions	Cm.	Cc.	Per cent. benzene	Per cent. paraffin
11–A	15	35	32.1	67.9
11–B	12	42	47.1	52.9
11–C	12	37	47.1	52.9
11–D	10	41	46.9	55.1
11–E	10	36	50.4	49.6
11–F	10	35	50.9	49.1

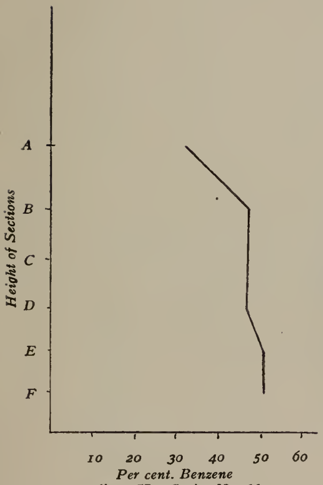

Fig. VII.—Series No. 11

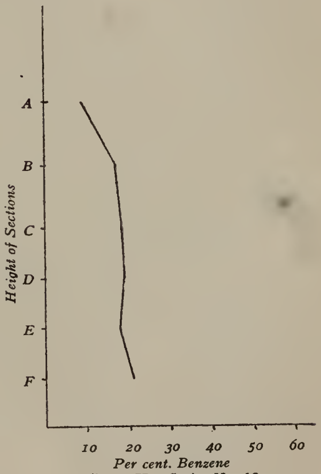

Fig. VIII.—Series No. 12

In all tubes up to Series No. 12 the oil was drawn up to a height under two feet nine inches. Although tubes five feet nine inches long were used, the quantity of oil placed in the reservoir was such as allowed only the lower half of the earth in the tube to become impregnated. In order to avoid the possibility of the more volatile oil evaporating into the dry earth above it, tubes of 2 feet 9 inches in length were used for Series No. 12 and No. 13. The curves representing the results from these series (pp. 81 and 83) show that this precaution failed to produce any noticeable difference in the proportion of benzene and paraffin oil or in the characteristic behavior of the fractions that were obtained by diffusion through fuller's earth.

Table XVIII—Series No. 12

Benzene, 20 per cent. Paraffin Oil, 80 per cent.

Rose to a height of 80 cm.

Fractions	Cm.	Cc.	Per cent. benzene	Per cent. paraffin
12–A	15	31	9.5	90.5
12–B	15	40	16.8	83.3
12–C	12	54	18.6	81.4
12–D	12	52	18.8	81.2
12–E	12	56	18.0	82.0
12–F	12	53	21.1	79.9

Table XIX—Series No. 13

Benzene, 75 per cent. Paraffin Oil, 25 per cent.

Rose to a height of 80.5 cm.

Fractions	Cm.	Cc.	Per cent. benzene	Per cent. paraffin
13–A	15	30	60.0	40.0
13–B	15	41	69.1	31.9
13–C	12	37	72.8	27.2
13–D	12	41	71.3	28.7
13–E	12	47	74.0	26.0
13–F	12	48	74.9	25.1

Series No. 14 was set up to test out the improved method of fractionating by means of the earth. Eight hundred cc. of a mixture of 20 per cent. benzene and 80 per cent. paraffin oil were drawn up through tightly packed fuller's earth, and six fractions of 50 cc. each were collected in the upper reservoir. The first of these was designated 14–A, and the last 14–F. The six fractions were separately analyzed and the results plotted in a curve (see p. 83).

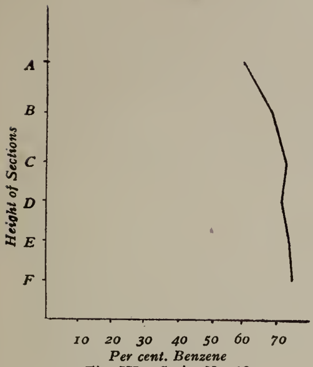

Fig. IX.—Series No. 13

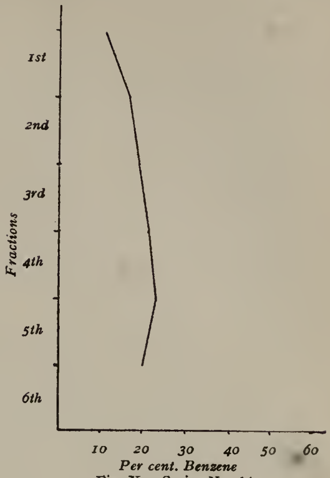

Fig. X.—Series No. 14

Table XX—Series No. 14

Benzene, 20 per cent. Paraffin Oil, 80 per cent.

Fractions	Cc.	Per cent. benzene	Per cent. paraffin
14–A	50	10.9	89.1
14–B	50	17.1	82.9
14–C	50	19.4	80.6
14–D	50	21.6	78.4
14–E	50	23.0	77.0
14–F	50	20.0	80.0

Extract of Earth Left in Tube

Fractions	Cm.	Cc.	Per cent. benzene	Per cent. paraffin
Upper half	70	215	15.9	84.1
Lower half	70	225	13.8	86.2

It was found that the proportion of benzene in the first fraction was the lowest, and that it gradually increased in the subsequent fractions. The curve above shows that the increase in benzene in the successive fractions is more gradual than when the oil was obtained by being expelled by water. There was, however, a marked increase in the amount of the benzene after the first 50 cc. had been drawn off. This corresponds to the increase indicated by the curves in every series that was run, and thus it appears that the new method of working gives the same results as the other methods of manipulation.

These results show that the degree of fractionation is not a question of the absolute height of the earth through which the oil passes, but of the relative height. The advantage, however, of using long tubes is that more material can be obtained and a greater number of fractions between the two extremes are possible.

FRACTIONATION OF CALIFORNIA OIL III

With a view to studying in some detail the fractionation of a heavy California petroleum, a tank of this material was secured from Kern County. It had a specific gravity of 0.9118 at 20°, and resembled in physical properties the California Oil I. A description of this oil, termed California Oil III, is found on page 60. In order to find the best conditions for securing large workable fractions of this oil, preliminary work was carried on by means of glass tubes so as to enable the investigator to observe the progress of the fractionation. The glass tubes measured 1.25 inches in internal diameter, and varied in length from two to five feet. The object of this was to find the length of tube which would give a maximum yield of workable fractions.

The tubes were filled with a fine-grained fuller's earth known as XXF clay. The method of packing these by ramming with a rod tipped with a rubber stopper was abandoned since this gave varying degrees of hardness, while strict uniformity was desired. It also failed to remove the cushions of air that persisted in remaining between layers of the earth, and these, it had been found in earlier work, were a grave source of trouble. Instead, the earth was run into the tubes until they were full. Then the tubes were tapped on their sides throughout their length until the earth failed to subside. More earth was added to fill in the space left vacant by the earth that had settled, and they were tapped again until further subsidence ceased.

With tubes packed as indicated above, the fractionation of the oil by suction was commenced. It was soon apparent that the amount of fractionation by using the fine-grained earth would be exceedingly small, and that it would possibly require four or five weeks' suction to bring the oil to the top of the longer tubes, so the effect of using a coarse-grained earth was suggested. Accordingly, fuller's earth of the size 30 to 60 mesh was secured. The tubes were packed uniformly by the method above described, and placed in the reservoirs. The pressure was reduced to 650 mm. of mercury. Even at this slight reduction in pressure, the oil was drawn up through the tubes, the products showing, however, no signs of fractionation. Accordingly, after repeated experiments, the tubes were allowed to stand 48 hours with no suction applied, and then the pressure on the top of the tubes was reduced to 730 mm. With this, the oil started to rise slowly and steadily through the earth, the uppermost part showing signs of marked fractionation. When the oil had risen to the height of about 18 inches, the pressure was reduced to 700 mm.; at a height of 3 feet, it was reduced to 650 mm.; and above 4.5 feet it was maintained at 600 mm. until all of the available oil was drawn over into the upper reservoirs. By use of the coarse-grained fuller's earth the time required for fractionation of a series of tubes was found to be from ten to twelve days. The fractions of oil that were drawn up and collected were classified on the basis of color. With this as a criterion, six distinctly different fractions were obtained, and these showed a wide range in color and specific gravity.

The total amount of these six fractions was, however, only 15 per cent. of the oil put into the lower reservoir, there being a loss of 85 per cent. due to the speedy darkening of the earth by the bitumen present in the petroleum. Results, with a brief description of the fractions obtained, are tabulated below:

Table XXI—Preliminary Fractionation of California Oil III

Fraction	Sp. gr.	Description
1	0.8364	Nearly colorless; pale green fluorescence
2	0.8449	Pale yellow; pale green fluorescence
3	0.8609	Yellow; quite fluorescent
4	0.8701	Light brown; strong fluorescence
5	0.8770	Brown; strongly fluorescent
6	0.8866	Dark brown; deep green fluorescence

These were the first results that were ever obtained with an oil of as high specific gravity and viscosity as this one, for all investigations carried on at room temperature with an oil of this high density had failed thus far to produce any results. When these six fractions were next examined as to their chemical properties, it was found that the diffusion through the earth had not only lowered the viscosity of the oil, removed the bitumen, and thereby greatly decreased the specific gravity of the oil, but it had also absorbed from the petroleum a large proportion of benzene and olefin hydrocarbons.

The amounts of the two last-named ingredients were ascertained by treatment of the oil with concentrated sulphuric acid. This did not determine the benzene and olefin hydrocarbons separately. It is fair to assume that the concentrated acid acted upon the other materials in the oil, but that it removed all the benzene and olefin hydrocarbons was conclusively proved by a method described later on.

The method by which the benzenes plus the olefins were determined was as follows: Ten cc. of each fraction were carefully measured from a burette. The light oils were shaken with three times their volume of concentrated sulphuric acid until no further diminution in the volume of the oil occurred. The shaking was accomplished in a machine that vibrated 400 times per minute. The bottles containing the oil thus treated were emptied into burettes, rinsed with a few cc. of acid and allowed to drain overnight. The oil not acted upon rose in this time above the acid, and could be read off and directly translated into percentages of paraffin hydrocarbons present.

This last statement is based upon the fact that paraffin hydrocarbons are not acted upon by cold, concentrated sulphuric acid, while the benzene and olefin hydrocarbons react with the acid to form sulphonic and alkylsulphuric acids, respectively. That the benzene and olefin hydrocarbons were entirely removed by two hours' agitation with a large excess of sulphuric acid was proved by the absence of these compounds in the oil after it had been acted upon. The test for benzene was the action of nitric acid to give nitro derivatives and the subsequent reduction to give amino compounds. The tests for olefin were the direct addition of bromine and the action of alkaline permanganate solution.

The treatment of the heavier oils with sulphuric acid was somewhat different from that of the light oils, in that in the case of the former the action of the acid produced a mixture so dark and viscous that the line of demarcation between the acid and the unabsorbed oil was invisible. Therefore, the sample of heavy oil was treated in one of the following ways:

I. It was mixed with twice its volume of pure paraffin oil that had been treated previously with concentrated acid until none of it was absorbed by further action of the acid upon it (see p. 75). The diluted oil was then shaken for five hours or more with three times its volume of acid until further diminution in volume of the oil ceased;[1] or

II. The sample was shaken with thirty cc. of sulphuric acid for two hours, and the mixture was thinned out by diluting with twenty cc. of the paraffin oil, shaken for a few minutes, drained into the burette, and the amount of benzenes and olefins present determined by difference between thirty cc. and the amount of oil unabsorbed by the acid. The methods of determining the sulphuric acid absorption gave results that were concordant to within 0.5 per cent. The accuracy of the analysis by this method was within one per cent., as was proved by analysis of known mixtures.

The percentages of benzene and olefin hydrocarbons that were found in the various fractions of the oil (see p. 86) were found to vary from 5.15 per cent. to 27.7 per cent., as shown in the following table:

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[1] For diluting the 10 cc. sample for analysis and shaking with 90 cc. of sulphuric acid, it was necessary to have a burette of over 120 cc. capacity. This was secured by blowing a bulb of 80 cc. at the lower end of a 50 cc. burette, leaving a volume of about 40 cc. above by which to read the amount of oil that was not acted upon.

Table XXII—Preliminary Determination of Benzenes and Olefins in California Oil III

Fractions	Per cent. benzenes and olefins
1	5.15
2	10.4
3	15.2
4	16.8
5	20.6
6	27.7

It is thus seen that the earth through which the oil passed exerted an absorptive effect upon the benzene and olefin hydrocarbons. This effect has been termed selective absorption or adsorption, by which is meant that the earth exerts an action upon the complex oil by which it retains an appreciable quantity of certain of its ingredients. It is not a filtration effect, for when the petroleum is drawn quickly through coarse or fine fuller's earth by means of low pressure, it filters through, depositing any solid matter that may be suspended, but being otherwise unaltered.

If the action of the earth is explained as a phenomenon of adsorption, the statement might be made that the separation of the bituminous material from the petroleum was by the coagulation and adhesion of the bitumen to the very extensive internal surface that the grains of fuller's earth possess. For it is a well-known fact that porous media like charcoal, dried clays, colloidal and finely divided metals, platinum sponge, etc., possess an enormous amount of surface energy, due to the forces that are active at their extensive surface, and that such substances show the phenomenon of adsorption to a marked degree. The separation of the bitumen, carrying with it the benzene hydrocarbons, the olefins, the sulphur and nitrogen compounds, may thus be regarded as a special case of adsorption.

If the bitumen is considered as existing in the colloidal condition, the effect of the internal surface of the fuller's earth could be explained as bringing about the coagulation of the colloidal bitumen into discrete particles which would carry with them all materials in the oil, save the paraffin hydrocarbons. That all the above-mentioned materials are held behind by the fuller's earth has been conclusively established by direct and indirect proof. In retaining the bitumen with benzenes, olefins, nitrogen and sulphur compounds and permitting the paraffin oils to diffuse through, the fuller's earth acts as a dialyzer, proving more or less impervious to the substances held in solution in the paraffin oils, but not so to the solvent itself.

Fractionation of California Oil III

For the more accurate study of the physical and chemical properties of the fractions obtained from this oil, large quantities of these fractions were necessary. Accordingly, a slight alteration was made in the apparatus employed, so as to be able to handle larger quantities. The tubes originally used measured 1.25 inches by 5.5 feet. It was now decided to test out tubes of greater diameter and length, and the size finally adopted was 2.75 inches in diameter by six feet in length. In order to be able to observe the behavior of the oil, a glass tube of the same size was joined in parallel with the tin tubes. With tubes of this diameter it was found that the best results were obtained by using very little suction, and by extending the suction over a period of about two weeks, as the yield of available fractions was found to increase through this method of working. This was ascertained by measuring the amounts of each of the fractions that were obtained from a single tube placed in a measured amount of petroleum. From this tube 14 distinct fractions were secured, the basis of distinction being the color of each. The amounts of each fraction and a brief description of the same are as follows:

Table XXIII—Preliminary Fractionation of California Oil III

Fraction	Amount Cc.	Description
1	35	Colorless, pale blue fluorescence
2	38	Colorless, pale green fluorescence
3	40	Pale yellow, pale green fluorescence
4	40	Yellow, pale green fluorescence
5	48	Yellow to deep orange-brown, increasing green fluorescence as fractions increased in sp. gr. and viscosity
6	45	
7	47	
8	60	
9	65	
10	63	Light to dark brown in transmitted light; fluorescence less pronounced, but still very noticeable
11	75	
12	85	
13	88	
14	110	

The total amount of available fractions was 839 cc. The amount of petroleum used was 3500 cc. The yield was 23.7 per cent.

It is seen from the above figures that the yield of heavier fractions is increasingly greater than that of the lighter oils. It is also to be noted that this slower method of working increased the total yield of available fractions from 15 per cent. to nearly 24 per cent. Fractions that were colored darker than the fourteenth were discarded as being contaminated with too much bitumen.

The fractionation of considerable quantities of California Oil III was then undertaken, and differentiation was made between the various fractions on the basis of specific gravity, a hydrometer small enough to fit into the upper reservoirs being used[1] to indicate the specific gravity approximately. The boiling points of the various fractions were taken at atmospheric pressure. Every fraction was found to be a mixture of oils, for not any of the boiling points remained constant, but, instead, rose through a range of 11 to 35 degrees. In determining the boiling points, 5 cc. of each fraction were taken. In order to get the boiling point of the greatest part of each, i. e., of that part which represented the average of the constituents, one cc. was distilled off, and the boiling point noted during the distillation of the next three cc. The boiling point of the last cc. was not taken. The distillates ranged from a colorless, thin oil with a smoky smell to a thick, dark brown oil of a very disagreeable odor resembling garlic.

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[1] The upper reservoirs were glass tubes 2.5 cm. × 16.5 cm. closed at one end. Two-hole rubber stoppers fitted in the tops which were flanged slightly to give air-tight connections.

The fractions from the California Oil III were termed 3–A, 3–B, etc. Those of a second fractionation were termed 3–A 1, 3–A 2, etc. The range of the fractions obtained was as follows:

Table XXIV—Fractionation of California Oil III

Fraction		Sp. gr.	Boiling point
1	3–A	0.8325	160°–195°
2	3–B	0.8347	172°–201°
3	3–C	0.8372	186°–219°
4	3–D	0.8462	210°–231°
5	3–E	0.8524	235°–260°
6	3–F	0.8551	247°–269°
7	3–G	0.8680	256°–280°
8	3–H	0.8781	268°–289°
9	3–I	0.8840	275°–310°
10	3–J	0.8885	284°–317°
11	3–K	0.8903	299°–326°
12	3–L	0.895	311°–328°
13	3–M	0.8972	317°–334°
14	3–N	0.8984	329°–340°
Crude petroleum		0.9118	105°–340°

These results show the very wide range in specific gravity between the first and last fractions of the petroleum under investigation. For comparison, the range of fractions obtained from a lighter Pennsylvania petroleum by Gilpin and Bransky are given in the following table:

Fractionation of Pennsylvania Petroleum

Fraction	Sp. gr.	Fraction	Sp. gr.
A–1	0.8250	D–2	0.8495
A–2	0.8287	D–3	0.8515
B–1	0.8367	D–4	0.8555
B–2	0.8392	E–1	0.8527
C–1	0.8413	E–2	0.8540
C–2	0.8460	E–3	0.8570
C–3	0.8488		
D–1	0.8470		

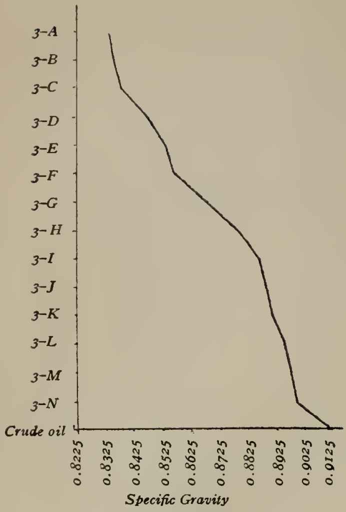

Fig. XI.—California Oil III

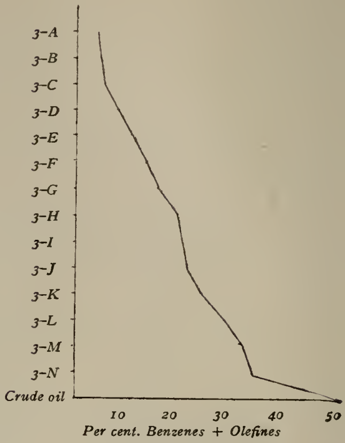

Fig. XII.—Sulphuric Acid Absorption of California Oil III

The range obtained by Bransky's method of working shows specific gravities varying from 0.8250 to 0.8570, as contrasted with the range of 0.8325 to 0.8984 obtained by the present investigator upon the heavy California oil.

Sulphuric Acid Absorption of the California Oil III

The sulphuric acid absorption was determined for the fourteen fractions. The method used was that described on pages 86 to 87. The results are tabulated with respect to the percentage of paraffin hydrocarbons in contrast to that of the benzene and olefin hydrocarbons taken together.

These figures show the great extent to which the diffusion through fuller's earth removes the benzene and olefin hydrocarbons. The first fraction consisted of nearly pure paraffin oils, reaching a degree of purity of 96 per cent., while, by contrast, the crude petroleum contained about 50 per cent. of paraffins.

Table XXV—Sulphuric Acid Absorption

Fraction	Per cent. benzenes and olefins	Per cent. paraffins
3–A	3.7	96.3
3–B	4.14	95.86
3–C	5.1	94.9
3–D	7.44	92.56
3–E	10.13	89.87
3–F	13.06	86.94
3–G	15.2	84.8
3–H	15.8	84.2
3–I	19.89	80.11
3–J	20.6	79.4
3–K	23.47	76.53
3–L	27.9	72.1
3–M	31.45	68.55
3–N	32.72	67.28
Crude petroleum	49.7	50.3

Bromine Absorption of California Oil III

In order to determine the amount of unsaturated or olefin hydrocarbons in the fourteen fractions of this oil, the quantity of bromine absorbed at room temperature (19°–23°) in the dark by a weighed amount of the oil was determined.

The method employed for the determination of the olefin content of the fractions was as follows: A weighed sample of the oil to be analyzed, about 0.6 gram for each determination, was dissolved in fifteen cc. of redistilled carbon tetrachloride. The vessel into which the solution was introduced was a 250 cc. Erlenmeyer flask with a ground glass stopper that fitted accurately and was sunk some distance into the neck of the flask so as to leave a gutter between the neck and the stopper. When the absorption of bromine was taking place, the gutter was filled with a couple of cc. of potassium iodide. It effectually prevented the escape of bromine vapor. The bromine was introduced in the form of a solution in pure carbon tetrachloride. The solution was made practically decinormal by dissolving 3.3 cc. of redistilled bromine in a liter of solvent. Its exact strength was determined by titrating against a known volume of a standard sodium thiosulphate solution. The bromine solution kept best in the dark, but frequent tests of its strength were necessary.

In determining the bromine absorption, a known quantity of the bromine solution was added to the solution of the oil in carbon tetrachloride. The amount added was more than twice that necessary to combine with the total amount of olefins present (as determined by a previous analysis). The flask was closed and shaken, the gutter filled with 2 cc. of a ten per cent. solution of potassium iodide, and the flask allowed to stand in the dark with occasional agitating for thirty minutes. Longer contact of the oil with the bromine gave substitution products as well as addition products, the former being indicated by the presence of hydrobromic acid. After thirty minutes, the flask was brought out of the dark, ten cc. of the potassium iodide solution were added, the flask closed and violently shaken, and the amount of iodine liberated by the excess of bromine present determined by titrating against the thiosulphate solution. Toward the end of the titration, a few cc. of a very dilute starch solution were added to indicate sharply the end point. Repeated shaking of the contents of the flask was necessary during the last part of the titration in order to free the iodine from its solution in the carbon tetrachloride. A blank determination was made parallel with each analysis in order to ascertain how much of the thiosulphate solution was exactly equivalent to the amount of bromine solution that was added. The results were translated directly into the percentage of olefins present in the various fractions and in the crude petroleum.

By the action of concentrated sulphuric acid on the oils, the percentage of benzenes and olefins together was ascertained. The action of bromine gave the percentage of olefins. In order to determine whether the difference between these results gave a value that represented the percentages of benzene alone, an investigation was carried out on the 1st, 5th, 9th and 14th fractions of the California Oil III. After being shaken for several hours with sulphuric acid, they were tested for the presence of benzenes and olefins, and blank results were obtained. Then fresh samples of these fractions were treated with an excess of bromine so as to brominate the olefins present, washed with water, dried and shaken with concentrated sulphuric acid for several hours. By this, an amount of the oil was absorbed which corresponded to the benzenes present. This amount, added to that secured by the action of bromine, gave the true percentages of benzenes and olefins together. The results, however, were in each case a little high, showing that the sulphuric acid must have acted upon the brominated oils, but the difference was not greater than 1.3 per cent. Since the sulphuric acid absorption method was accurate to within one per cent., it was concluded that the difference between the percentages of the oil absorbed by sulphuric acid and that acted upon by bromine could be taken to represent the amount of benzene hydrocarbons present.

The results that justified this conclusion are here given:

Table XXVI

Fraction	Per cent. benzenes	Per cent. olefins	Sum of columns 2 and 3	Per cent. benzenes and olefins by sulphuric acid absorption
3–A	1.09	2.79	3.88	3.7
3–E	5.35	5.05	10.4	10.13
3–I	8.72	12.46	21.18	19.89
3–N	14.03	19.35	33.38	32.72

In the table below, the percentages of the various hydrocarbons present in the oils investigated are given. In the first column are given the designations of the various fractions; in the second are given the mean values of the percentages of the olefins found by determining the bromine absorption (duplicate determinations made in every analysis); in the third are given the percentages of benzenes and olefins taken together, and determined by the sulphuric acid absorption method; in the fourth are given the percentages of benzenes determined by difference between the second and third columns.

These results demonstrate the selective absorption of the fuller's earth in its action upon the olefin hydrocarbons. As is indicated above, the proportion of olefins in the crude oil is

Table XXVII—Proportion of Various Hydrocarbons in Fractions of California Oil III

Fraction	Per cent. olefins	Per cent. benzenes and olefins	Per cent. benzenes
3–A	2.79	3.7	0.81
3–B	3.25	4.14	0.76
3–C	3.62	5.1	1.48
3–D	4.06	7.44	3.38
3–E	5.05	10.13	5.08
3–F	5.84	13.06	7.22
3–G	7.44	15.2	7.76
3–H	8.43	18.8	7.37
3–I	12.46	19.89	7.43
3–J	13.44	20.6	7.16
3–K	14.66	23.47	8.81
3–L	14.81	27.9	13.19
3–M	18.34	31.45	13.11
3–N	19.35	32.72	13.37
Crude petroleum	28.24	49.7	21.47

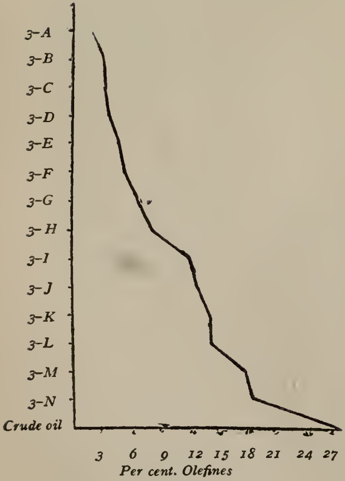

Fig. XIII.—California Oil III

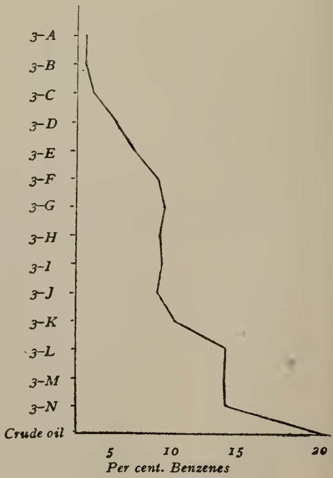

Fig. XIV.—California Oil III

28.24 per cent. In a single fractionation this is reduced to 2.79 per cent. in the first fraction obtained. The gradual increase in the proportion of olefins as the specific gravity of the fractions increases is parallel to the gradual increase, in successive fractions, of all the compounds in the petroleum thus far studied, i. e., of the sulphur compounds, nitrogen compounds, benzene hydrocarbons and olefin hydrocarbons. The results, when plotted in the form of curves, show that there is a noticeable parallelism in selective action of the fuller's earth upon the compounds above mentioned. The curves are found on pages 92 and 96.

In order to determine to what extent the olefins could be removed by further filtration through fuller's earth, a liter of Fraction 3–I was refractionated by means of a tube of smaller diameter. The nine fractions that were obtained were analyzed for their olefin content. The results were as follows:

Table XXVIII—Second Fractionation of California Oil III
(Refractionation of 3–I)

Fraction	Sp. gr.	Per cent. olefins
3–I 1	0.8661	8.55
3–I 2	0.8685	8.93
3–I 3	0.8740	10.06
3–I 4	0.8751	10.82
3–I 5	0.8759	10.77
3–I 6	0.8773	11.40
3–I 7	0.8782	11.67
3–I 8	0.8801	11.79
3–I 9	0.8807	11.89
3–I 10	0.884	12.06

These results demonstrate that a further removal of bituminous material is possible by refractionating a heavy fraction, for there was a slight loss of color occasioned by the diffusion through the earth. Only a part of the olefins was removed, however, by this second fractionation, and the reduction in viscosity was also very slight.

Efforts were made to determine the effect of shaking fractions of oil with large amounts of fuller's earth. Accordingly several portions of Fraction 3–E were shaken with varied quantities of fuller's earth for different periods of time. First, a quantity was shaken with three times its weight of earth for 30 hours and separated from the earth by suction. It was analyzed, with the following results:

Table XXIX—Fraction 3-E Shaken with Three Times Its Weight of Earth

Time in hours	Sp. gr.	Per cent. olefins	Color
20	0.8305	4.01	Yellow
0	0.8524	5.05	Pale orange

When shaken with one-half its weight of earth for periods ranging from 10 to 50 hours, the following results were obtained:

Table XXX—Fraction 3-E Shaken with One-half Its Weight of Earth

Time in hours	Sp. gr.	Per cent. olefins	Color
0	0.8524	5.05	Pale orange
10	0.8524	5.08	Pale orange
20	0.8521	5.00	Pale orange
30	0.852	5.00	Pale orange
50	0.8513	4.90	Same color, but slightly less fluorescence

These results show that the time that an oil is in contact with fuller's earth is of little or no importance as a factor in determining to what extent the earth absorbs certain ingredients from it. The important factor is the amount of earth with which it comes in contact. These experiments substantiate, then, the deductions that are given on page 88 *et seq.*, i. e., that it is the amount of surface of the earth to which the oil is exposed that determines the extent of its absorptive action.

This is in line with the action of those substances whose surface energy is capable of affecting a colloid. That the bitumen in the petroleum investigated exists in this form was proved by the following:

1. There was effected an actual separation of the petroleum into two distinct layers when an electromotive force of 110

volts was impressed upon parts of the oil separated by an unglazed porcelain septum. In order to make the oil conduct the current, one portion was shaken for several hours with one-fourth its volume of a 20 per cent. solution of hydrochloric acid, and another with an equal amount of a 20 per cent. solution of potassium hydroxide. The emulsions formed in this way proved poor conductors, but were sufficiently good to enable the bitumen partially to precipitate out as a brown layer of a very viscous liquid, containing no mineral residue. Its form indicated that the bitumen was held in the original petroleum as a colloid—that type that has been named by Oswald an emulsoid.

2. The high temperature coefficient of viscosity of California petroleum, as shown by earlier experiments (p. 63, Table I), is one of the most marked characteristics of emulsoids, i. e., that type of colloid solution in which the colloid is a liquid in a state of minute subdivision in a liquid medium.

3. The oil and bituminous material that were held back by the fuller's earth could not be removed by mechanical means. For, after the earth had been extracted with ether and carbon tetrachloride until no more could be extracted, it yielded a small quantity of oil upon distillation. This showed that the bituminous material that was in the oil had undergone a change of condition when it was adsorbed by the earth.

SUMMARY

1. The diffusion of petroleum through fine-grained fuller's earth failed to effect the fractionation of the petroleum when the latter was of specific gravity as high as 0.912 at 20°. Raising the temperature of such an oil to 75° made fractionation possible.

2. The effect of such a diffusion of a petroleum containing compounds of sulphur is to separate out the light fractions of the oil containing smaller proportions of sulphur than are found in the original petroleum.

3. The effect of fractionating by means of diffusion through fuller's earth of a petroleum containing nitrogen compounds is to remove the nitrogen compounds from the oil that diffuses

upward through the earth, and to cause them to concentrate in the earth through which the oil has passed.

4. Mixtures of benzene and paraffin oil, when fractionated by capillary diffusion through fuller's earth, give fractions that have marked general characteristics, both chemical and physical, based on the proportions of benzene and paraffin oil in each.

5. The fractionation of a petroleum rich in benzene and olefin hydrocarbons by the diffusion through fuller's earth gives fractions in which the proportions of benzene and olefin hydrocarbons increase regularly with the increase in specific gravity of the successive fractions.

6. An explanation of the above phenomena was found in the conception of the petroleum as an emulsoid, and in the action of the fuller's earth as a dialyzing septum, permitting the free passage of the paraffin oils, and causing by its extensive surface the adsorption and coagulation of the bituminous material, carrying with it the sulphur and nitrogen compounds and the benzene and olefin hydrocarbons.

JOHNS HOPKINS UNIVERSITY
May, 1913

REPORT

THE RELATION BETWEEN ELECTRIFICATION AND CHEMICAL REACTIONS AND THE PROPERTIES OF CONDENSATION NUCLEI

1. Phenomena of Condensation of Supersaturated Vapors on Ions. 2. Ionization and Chemical Action. 3. Ions of Small Mobility. 4. The Charging of Neutral Centers and Their Properties. 5. Molecular Aggregates Produced in Gases by Sudden Cooling. 6. The Production of Nuclei. 7. Positive Rays. 8. The Dissociation of Molecules by Moving Ions and the Dynamics of Chemical Reactions in Gases.

Ever since the discovery of the phenomena of electrolysis and the wonderful work of Faraday, scientists have assumed that electrical forces probably play a very important role in the processes involved in chemical reactions. The recent development of our knowledge of the ionization of gases and the phenomena of radioactivity has very greatly strengthened the view that electrons and ions may be products taking part in chemical reactions and the view has been so extended by Thomson and others as to attribute chemical valency to the presence or absence of one or more electrons from an atom or radical.

In order to apply a theory of this kind it is necessary to unravel completely the whole mechanism that is required in order that a given chemical reaction may take place. The experimental evidence shows very clearly that chemical reactions are not nearly as simple as represented in our text-books and that we probably know the exact mechanism in only a few cases.

The relation between electrification and chemical reactions can be considered in three different fields.

(*a*) The study of the processes taking place in solutions led to the atomic theory of electricity and proved a very intimate quantitative relation to exist between the atoms and radicals and the charges which they carry. Investigations in this field of research do not permit us to deal with individual atoms and molecules. In this branch of research we have never isolated quantities of matter containing less than hundreds and perhaps millions of atoms. Indirect evidence in many cases points to the view that molecules in solutions are frequently aggregated together, so that chemical reactions under these conditions must necessarily be much more complex than in gases, where molecules usually exist as independently moving particles. As the study of chemical reactions in solutions has not given us any detailed information concerning the dynamics of chemical reactions, we will pass to a consideration of the phenomena taking place in gases at atmospheric pressure.

(*b*) The early work on ionization indicated that the liberation of electrolytic gases from solutions, the combustion of substances in flames, the oxidation of solids and liquids, and many other phenomena were associated with more or less intense electrification. Naturally, it was expected that a thorough study of these phenomena would lead us to a knowledge of the role played by electrons and ions in various chemical reactions. In order to discuss these phenomena we will have to take up briefly the condensation of vapor on various kinds of nuclei and ions and the properties of "vapor dust" and the various types of ions. The result of this inquiry will show that the processes that take place in flames are very much more intricate than we had at first expected and that as yet we know only a few reactions where it seems that electrons and ions take a direct part.

(*c*) The third field is by far the simplest, and it is in this region that some of the most fundamental of recent discoveries have been made. This field is being most ingeniously explored by J. J. Thomson and most remarkable electrical properties are being discovered concerning the different kinds of ions that constitute positive rays. Stark and others are discovering the nature of the carriers of different types of spectra, so that in the future we shall probably be able to identify the nature of particles in flames, sparks and arcs by the kind of light which they emit. Strutt, Langmuir, Kirkby, and others, are determining the very mechanical processes involved in certain types of chemical reactions taking place at low gas pressures. It seems probable that the new chemistry will deal with atoms, molecules, ions and electrons individually, and that the chemical constants will be calculated as possessing certain statistical values based on the kinetic theory of matter, heat and electricity. In taking up the relation between ionization and chemical reactions we will consider briefly the properties of ions, condensation nuclei and molecular aggregates.

Phenomena of Condensation of Supersaturated Vapors on Ions

Aitken,[1] Coulier,[2] Kiessling,[3] and others, showed that the clouds produced by the lowering of temperature resulting from small adiabatic expansions of damp, dusty air failed to appear if the dust was removed by filtration. The drops in the cloud collected about the dust particles and did not pass through dimensions comparable to that of molecules, where the effect of surface tension would presumably lead to intense evaporation. Phenomena of condensation led R. von Helmholtz, Richarz, and others, to believe that ions could also act as nuclei. The method, used by C. T. R. Wilson,[4] of suddenly cooling a moist gas by adiabatic expansion, so that the gas becomes supersaturated, shows that negative and positive ions act as condensation centers.

When the filtered gas saturated with water vapor is ionized, no cloud is formed until the expansion is 1.25; at this expansion condensation begins to take place on the negative ions. (It would be interesting to work with the proper vapor and the proper pressure to find what expansions would be necessary for ions of different sizes.) The intensity of the rays producing the ionization has no effect on changing the value 1.25. Clouds can be produced several seconds after the ionizing rays have been cut off. The proof that the condensation takes place about the negative ions lies in the fact that the droplets in the fog are all negatively charged and that the production of these fogs is prevented by the removal of the ions.

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[1] Nature, **23**, 195, 394 (1880).

[2] J. pharm. chim., **22**, 165 (1875).

[3] Naturw. Verein. Hamburg-Altona, **8**, 1 (1884).

[4] Phil. Trans., **189**, 265 (1897).

After the production and evaporation of a dense fog by an expansion between 1.25 and 1.38, it is found that for a short time drops can be produced by an expansion less than 1.25. The evaporation of the dense fogs has apparently left nuclei (possibly little drops of water) that act like dust particles. Positive ions begin to act as nuclei when the expansion is 1.31 or greater. For eightfold supersaturations dense clouds are formed without the action of an ionizing agent. These droplets are uncharged. J. J. Thomson gives their probable radius as 0.5×10^{-7} cm., this being slightly larger than the size of the drop that forms about an ion (0.3×10^{-7} cm. radius). The amount of supersaturation necessary for these kinds of fogs is the same in air, oxygen, hydrogen and carbon dioxide. Intense ultraviolet light produces clouds in air and oxygen without the necessity of any expansion at all. These clouds are very fine and may last for hours after the light has been removed. This may be due to the formation of hydrogen peroxide or some other substance which lowers the vapor pressure of the drops.

(Much interesting work remains to be done upon the condensation of various vapors at various pressures and temperatures upon ions. Electrons could be experimented upon at low temperatures, the vapor and expansion being suitably chosen. Ions of different kinds, such as recoil atoms, can be used as condensation centers.)

C. T. R. Wilson[1] has succeeded in making visible the tracks of ionizing particles through a moist gas, by condensing water upon the ions immediately after their liberation. The cloud chamber is 16.5 cm. in diameter and 3.4 cm. high, the sides being of glass coated on the inside with gelatin. A Leyden jar discharge through mercury vapor is used to illuminate the clouds formed during the expansion. The spark is produced at a definite interval after the formation of the cloud.

The tracks of the α-particles, as photographed by the above method, are narrow and sharply defined when the α-particles have been shot out just before the expansion. Trails have been photographed for the emanation products in a gas as well as from solids. The tracks are straight over the greater part of the length of the path, but near the ends of the path they are nearly all bent, often abruptly. The bent portion may be 2 or 3 mm. in length. Sometimes the collision of an α-particle seems to give sufficient energy to the particle struck to cause it to ionize by collision, i. e., makes a recoil ray. The formation of these recoil rays should give us considerable knowledge of the nature of the collisions and of the colliding particles. Some α-rays show a gradual bending throughout a large portion of the path.

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[1] P. Roy. Soc., A, **85**, 285 (1911); **87**, 277 (1912).

The β-particles leave tracks that are straight at first and later become curved with many sudden changes in direction. Over considerable distances the ions appear in pairs, but now and then 20 or 30 ions appear together in a closely packed group. The groups are similar to those produced by secondary cathode rays generated by X-rays. The negative ions give rise to a densely packed cluster while the positive ions are more scattered out by the action of the electric field of the expansion chamber. Omitting the clusters, the number of ions is about 32 per cm. length of path at atmospheric pressure. Including the clusters, the number of ions is about double the above number. The clusters may be due to slow cathode rays produced by the β-particles. While α-particles show both a gradual and a sudden bending of their paths, the β-particles show a bending which is generally gradual or cumulative.

The photographs of X-ray ionization do not indicate any effect produced by the X-rays except that of causing secondary cathode rays. Wilson has used a heterogeneous X-radiation and hence has found the secondary cathode rays possessing different lengths of path varying from 0.5 to 1 cm. It would be interesting to find whether a homogeneous X-radiation gave cathode rays of the same velocity.

The secondary cathode rays showed sudden and cumulative changes in regard to the direction of their paths, the latter being the more important. Abrupt deflections occur frequently through angles of 90° or more. The bending is greater near the end of the trail and the end itself is enlarged into a kind of head, possibly due to the path of the corpuscle becoming very irregular. About 5 mm. from the end, the number of ions produced per cm. of track at atmospheric pressure is about 400. At the last 0.5 mm. of one path 4320 ions were counted in one case. The rays appear to start in all directions. The photographs indicate the number of positive and negative ions to be the same.

In considering the chemical effects of the various ionizing radiations it is necessary to know the process of ionization and the nature of the collisions. Methods such as Wilson's should provide a method of finding how ozone, oxides of nitrogen, hydrogen peroxide, etc., are produced by α-, β- and γ-rays.

Condensation in Gases Saturated with Water Vapor

(V_1 is the volume of the gas before expansion and V_2 the volume after expansion. S is the supersaturation of the water vapor after the expansion.) Gas under normal conditions:

	Rainy condensation		Misty condensation	
Gas	V_2/V_1	S	V_2/V_1	S
Air	1.252	4.2	1.38	7.9
O_2	1.257	4.3	1.38	7.9
N_2	1.262	4.4	1.38	7.9
CO_2	1.365	4.2	1.535	7.3
Cl_2	1.3	3.4	1.45	5.9
H_2	1.3	3.4	1.38	7.9

Condensation in Air Ionized by X- and γ-Rays

Observer	Vapor	Ion	V_2/V_1	S
Wilson	Water	—	1.25	4.15
“	Water	+	1.31	5.8
Laby	Ethyl acetate	+	1.48	8.9
“	Methyl butyrate	+	1.33	5.3
“	Methyl isobutyrate	?	1.35	5.2
“	Propyl acetate	+	1.31	5.0
“	Ethyl propionate	?	1.41	7.8
“	Formic acid	?	1.78	25.1
“	Acetic acid	+	1.44	9.3
“	Propionic acid	?	1.34	9.4
“	Butyric acid	?	1.38	15.0
“	Isovaleric acid	?	1.22	6.0
Przibram	Methyl alcohol	+	1.25	3.1
“	Ethyl alcohol	+	1.17	2.3
“	Propyl alcohol	?	1.18	3.0
“	Isobutyl alcohol	?	1.20	3.6
“	Isoamyl alcohol	+	1.22	5.5
“	Chloroform	+	1.54	3.0

Besson[1] has studied the clouds produced in carbon dioxide saturated with water vapor. The following are some of the results obtained by him:

Expansions below 1.30	A few drops
Expansion between 1.30 and 1.32	A few additional drops
Expansion 1.332	Light rain, not very dense
Expansion between 1.332 and 1.40	Gradual increase of the rain
Expansion between 1.41 and 1.44	Rapid increase of the rain

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[1] Compt. rend., **154**, 342 (1912).

Expansion between 1.453 and 1.50	Thick clouds that remain in suspension for a long time. Slow increase in the intensity of the cloud with an increase of expansion
Expansion 1.51	Very thick fog
Expansions above 1.51	The appearance of the fog is not changed

The action of X-rays causes the appearance of rain for an expansion of 1.30, as in the case of air. The addition of a small amount of air results in the appearance of rain for an expansion of only 1.30.

Ionization from Flames

The gases that come from flames of coal gas (whether luminous or not), oxyhydrogen, alcohol, carbon monoxide, etc. (but not of ether), even when the flames are at some distance and the gases have been cooled, show a very considerable conductivity for some time. This conductivity is due to the presence of ions. The ions stick to any dust or small particles that may be in the gas, and then move so slowly that their rate of recombination is very small. McClelland[1] has shown that the mobility of the ions decreases very rapidly as the distance from the flame increases. For the production of this ionization high temperature as well as chemical combination is necessary, and it is possible that chemical reactions themselves are not the cause of the ionization. For instance, hydrogen and chlorine do not conduct even when combining under the influence of ultraviolet light.[2]

From the work of Pouillet,[3] Neyreneuf,[4] Holtz[5] and others among the early workers, it was shown that in a coal-gas flame, where the gas comes in contact with the air, and where combustion is most rapid, the electrification is positive, and is attracted by a negatively charged electrode. The interior of the flames, consisting largely of unburned coal gas, has an excess of negative electricity. Important work upon the electricity developed in flames has been done by Giese[6] and others, an account of which is given by Wiedemann.[7] Franck and

[1] Phil. Mag., **46**, 29 (1898).

[2] Thomson: P. Camb. Phil. Soc., **11**, 90 (1901).

[3] Ann. chim. phys., **35**, 410 (1827).

[4] *Ibid.*, [5] **2**, 473 (1874).

[5] Carl Repert, **17**, 269 (1881).

[6] Ann. chim. phys., **17**, 1, 236, 519 (1882).

[7] Elektricität, **14**, 8, Chap. 4.

Pringsheim[1] have burned hydrogen in chlorine. The mobility of the positive ions thus formed is many times greater than that of the negative ions. Electrons do not appear to exist. The anode fall is greater than the cathode fall, and the unipolar conductivity of the flame is the reverse of that of ordinary flames. Sodium chloride does not give any coloration to such a flame.

The introduction of salt vapors into flames greatly increases their conductivity, especially when the salt is introduced at the cathode. Arrhenius[2] and Wilson[3] have studied the influence of various salts on the conductivity of flames by introducing solutions of the salt into the coal gas by means of a Gouy sprayer. The conductivity of the salt was obtained by getting the difference of the conductivity before and after the salt was introduced. When the concentration of the salt was small, equivalent solutions of all salts of the same metal gave approximately the same conductivity to the flame. The conductivity given by different salts in flames at the same temperature and at the same concentration is as follows:

	Chlorides			Nitrates		
Potential diff.	5.60	0.795	0.237	5.60	0.795	0.237
	Current			Current		
Caesium	123.0	60.5	22.2	303.0	115.0	36.6
Rubidium	41.4	26.4	11.3	213.0	82.4	25.9
Potassium	21.0	13.4	5.75	68.4	29.3	9.35
Sodium	3.49	2.45	1.15	3.88	2.67	1.32
Lithium	1.29	0.87	0.41	1.47	0.99	0.53
Hydrogen	0.75	...	0.27			

G. C. Schmidt[4] considers that the vapors of the halogen salts of zinc, cadmium, aluminium and ammonium conduct electricity while those of mercury, tin, arsenic and organic substances are nonconductors. The conductivity of cadmium salts decreases with the time until a constant value is reached. The other salts usually show an initial increase and then behave like the cadmium salts. The conductivity increases rapidly with rise in temperature and with decreasing pressure.

The mobility of the negative ion in flames at 2000° C. is about 1000 and is independent of the salt in the flame. The mobility of the positive ions of caesium, rubidium, potassium, sodium and lithium is about 62. In heated air, at about 1000° C., Wilson found:

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[1] Verh. d. physik. Ges., **13**, 1911.

[2] Ann. Physik, **42**, 18 (1891).

[3] Phil. Trans., A, **192**, 499 (1899).

[4] Ann. Physik, **35**, 401 (1911).

	Mobility
Negative ion	26.0 cm./sec.
Positive ion, Li, Na, K, Rb, Cs	7.2 cm./sec.
Positive ion, Ba, Sr, Ca	3.8 cm./sec.

The experiments of Gold,[1] Wilson,[2] etc., leave no question but that at high temperatures the negative ion is the electron. The problem as to the nature of the positive ion is much more difficult. Marx[3] obtained mobilities of about 250, while Moreau[4] deduced a value of about 80 at 2000° C.

Experiments have been made by Moreau[5] to determine the mass and charge of the negative ion and its rate of diffusion through sheets of metal. The value of the mass obtained is between that of the corpuscle and the hydrogen atom. It is probable that the negative ion exists part of the time as a negative electron, and part of the time as a negative electron combined with one or more molecules. Negative ions diffuse very rapidly through sheets of metal, the sheets of metal playing the same role towards ions as a porous wall does towards a gas. The phenomena obey the law of Graham. A metal sheet in this case plays the role of a semipermeable membrane, it being permeable only to negative ions. By using these sheets to determine the mass of the negative ion, knowing its coefficient of diffusion, Moreau obtains a value for the charge of the negative electron which is 4.2×10^{-10}, agreeing well with the other measurements of this quantity.

Lusby[6] measures the current between electrodes placed horizontally, one above the other, in the flame, the upper plate being positive. A bead of salt is then placed in the flame just beneath the upper electrode. When the potential difference is great enough to drive back the positive ions against the uprush of the gas, the current suddenly increases. Knowing this critical voltage, the minimum electric force in the flame can be determined, and, knowing the velocity of the flame, the ionic mobility is obtained.

The following table gives the saturation current in a pure Bunsen flame between electrodes 3 cm. apart. The values are for the total current between the electrodes whose effective area was 2 sq. cm. The relation between the temperature and the logarithm of the current is practically a linear one:

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[1] P. Roy. Soc., A, **79** (1907).

[2] *Ibid.*, A, **82**, (1909).

[3] Ann. Physik, **2**, 790 (1900).

[4] Ann. chim. phys., **1903.**

[5] *Ibid.*, **18**, 433 (1909).

[6] Phil. Mag., **22**, 775 (1911).

Absolute temperature	Saturation current
1150° C.	35×10^{-9} Amp.
1220° C.	51
1300° C.	107
1370° C.	150
1450° C.	230
1700° C.	600
1950° C.	1500

The potential gradients, as obtained by Lusby,[1] are given in the following table: This shows (1) a small anode fall; (2) a region of small constant electric force where the quantities necessary for a determination of the mobility are obtained; (3) a sudden cathode drop. The form of the several curves plotted from these data show the effect of change of temperature.

Mobilities of Positive Ions

(*a*) Monovalent metals (*b*) Divalent metals

Absolute temperature	Minimum E volts/cm.	Gas velocity	$K+$ mobility	$K_1\sqrt{\theta}$
1950	0.61	214	350.0	100.0
1700	0.65	210	320.0	93.0
1450	0.71	206	290.0	86.0
1370	1.58	181	115.0	83.5
1300	3.87	164	42.5	81.5
1220	(*a*) 7.18 (*b*) 9.16	183	(*a*) 25.5 (*b*) 20.5	79.0
1150	(*a*) 17.0 (*b*) 3.3	207	(*a*) 12.2 (*b*) 6.2	77.0

Metallic particles may be introduced into flames, and the electrification can be studied by means of exploring electrodes charged to a high potential (as, for instance, by means of a friction electrical machine). Metallic vapors are electropositive in the inner cone of a Bunsen flame, and are partially or wholly neutralized in the outer cone (as is lithium). Sodium, potassium and rubidium are only partly neutralized, while caesium remains strongly positive. According to Irving,[2] the principal series lines are emitted by regions of the metallic vapor that are either positive or neutral.

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[1] P. Camb. Phil. Soc., **1**, 26 (1910).

[2] Physic. Rev., **29**, 243 (1909).

Flames are sometimes used for the rectification of high-tension alternating currents. If two electrodes, one of which is very small with respect to the other, be placed in a flame without solid matter in suspension and connected to a high-voltage alternating current, the current which passes will be unidirectional and will flow from the large to the small electrode. The effect is increased, according to Cathiard,[1] if the small electrode consists of fine points. He obtained a slightly luminous arc under these conditions, the point of which made a moving contact with the large positive electrode. Hydrogen, alcohol and illuminating gas flames gave the above effect. The small electrode consisted of a cylindrical carbon ring about 5 mm. in diameter. With voltages of from 2000 to 10,000 at 40 cycles and an electrode distance of about 8 mm., a current of 0.03 ampere was obtained. Above this voltage arcing took place and no rectification was obtained. Oscillograph examinations show the effect is due to a disintegration of the cathode.

Ionization and Chemical Action

Many chemists and physicists had noticed various electrical effects during chemical reactions, but very little of any importance was known until the theory of the ionization of gases was advanced. Among the early workers along this line was Townsend,[2] who showed that the ionized gas produced by the action of sulphuric acid on iron retained its electrification after passing through tubes of packed glass wool, thus proving that the electrification was not carried by coarse spray. Townsend found that the chlorine liberated by the action of hydrochloric acid on manganese dioxide is positively electrified, as is also oxygen produced by heating potassium permanganate.

Kosters[3] and Townsend have shown that many gases liberated in electrolysis are charged. The former attributes many of the results to the bubbling of the gases through the electrolyte. For example, hydrogen given off by the electrolysis of sulphuric acid at 40° or 50° has a considerable positive charge, whereas the charge of the oxygen is very small. When these gases are evolved from a solution of caustic potash, the hydrogen is but slightly electrified whereas the oxygen possesses a large negative charge which increases as the temperature is raised.

Townsend[4] found that the electrified gases had the power of producing clouds if they entered a vessel containing water vapor, although the air was not saturated with water vapor and the temperature was not lowered. H. A. Wilson[1] has shown that the spray from solutions of salts or acids, of sugar or glycerol, when filtered through sulphuric acid and passed into a damp atmosphere, produce a cloud.

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[1] Compt. rend., **146**, 20, 229 (1908).

[2] P. Camb. Phil. Soc., **9**, 345 (1988); Phil. Mag., [5] **45**, 125 (1908).

[3] Ann. Physik, **69**, 12 (1899).

[4] P. Camb. Phil. Soc., **9**, 345 (1897).

Although the sulphuric acid may rob the drops of water, still the neutral center of salt probably passes on, and when it enters into the damp atmosphere, the water condenses about the salt and forms a drop of solution. As the vapor pressure for these solutions is smaller than for pure water, they do not evaporate, although the gas is not saturated with water vapor.

Bloch[2] has measured the mobility of the ions formed when hydrogen is produced by treating zinc with hydrochloric acid, when carbon dioxide is produced by treating marble with hydrochloric acid and when oxygen is generated by heating potassium permanganate. His value was about 0.001 cm. per second, and, assuming Stokes' law, his value for the radius of the ions is 2.5×10^{-7}.

The ionization of air and other gases passed over phosphorus has been studied by Barus,[3] Schmidt,[4] Harms,[5] Bloch[6] and others. Barus found that hydrogen passed over phosphorus is not ionized. Bloch has shown that the mobility of the ions is about 0.001 cm. per second, the radius being about 10^{-6} cm. and the coefficient of recombination about a thousandth that of the ions produced by X-rays. The ions seem to consist of oxides of phosphorus condensed about the ordinary small ions.

Elster and Geitel[7] have shown that air passed over hot sulphur, even at a very high temperature, is not ionized.

Becker[8] considers that the size of nuclei in a gas containing ozone and a vapor such as ammonia depends on the concentration of the ozone and of the vapor.

Le Bon,[9] Miss Gates,[10] and Kalahne[11] have shown that the hydration and dehydration of certain salts (quinine sulphate) is accompanied by ionization. Driving off the water of crystallization from many salts by heating is usually accompanied by ionization.

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[1] Phil. Mag., [5] **45**, 454 (1898).

[2] Ann. chim. phys., [8] **4**, 25 (1906).

[3] Experiments with ionized air, Washington, 1901.

[4] Ann. Physik, **10**, 704 (1903).

[5] Physik. Z., **4**, 111 (1902).

[6] Ann. chim. phys., [8] **4**, 25 (1905).

[7] Ann. Physik, **39**, 321 (1890).

[8] *Ibid.*, **36**, 215 (1911).

[9] Compt. rend., **130**, 891 (1900).

[10] Physic. Rev., **18**, 135 (1904).

[11] Ann. Physik, **18**, 450 (1905).

Beattie[1] and Garrett and Willows[2] have mixed sodium chloride and iodine together on a plate, and heated the mixture to about 300°. The result is an emission of large numbers of positive and a smaller number of negative ions by the salt. The latter investigators find that by heating zinc chloride or iodide, in platinum vessels to 350°, large quantitites of ions are given off, and as the temperature is raised, the number of emitted ions is increased. If the zinc iodide was kept at a constant temperature, the rate of emission of ions diminished as an exponential function of the time, and at 360° the rate of production of ions fell to half value in 41 minutes. The mobility was 0.0017 cm. per second. Many salts heated to redness give off more ions than the corresponding metals would do, and the excess ions may be either positive or negative, according to the nature of the salt.

Under some conditions it seems that chemical reactions may be accompanied by the emission of electrons. Haber and Just[3] claim that the action of phosgene on clean sodium-potassium (caesium, potassium or lithium) surfaces in the dark at ordinary temperatures and in high vacua is accompanied by the emission of electrons. Bromine acts in the same way as phosgene.

Broglie and Brizard[4] conclude from a series of experiments that chemical action itself is not accompanied by any ionization in the surrounding gas. They would explain the ionization in the neighborhood of a chemical reaction as being due to heating (incandescent metals and metallic oxides emit ions; and silver[5] produces ions at as low a temperature as 200°), by the formation and breaking of bubbles, or by the decrepitation of crystals, etc. The following table gives a summary of the results obtained for various chemical reactions:

A. The fumes produced in moist air by phosphorus trichloride and pentachloride, arsenic trichloride, stannic chloride, antimony pentachloride, silicon fluoride, hydrochloric acid, hydrobromic acid, fuming nitric acid, fuming sulphuric acid, anhydrous sulphuric acid, ammonia gas in the presence of chlorine, hydrochloric acid gas, nitric acid gas or ozone do not produce charged particles. When exposed to the rays from radium, many of the particles are given a unit charge. In

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[1] Phil. Mag., **48**, 97 (1899); **11**, 422 (1901).

[2] *Ibid.*, **8**, 437 (1904).

[3] Ann. Physik, **36**, 308 (1911).

[4] Le Radium, **7**, 164 (1910).

[5] Strutt: Phil. Mag., **1902**, 98.

A. Reactions without the breaking of a liquid surface	Reactions between gases at low temperatures	No conductivity
	Double decomposition. Formation of precipitates in a liquid	No conductivity
	Dry decomposition	No conductivity
B and C. Reactions involving the breaking of a surface	Breaking of an inactive surface by bubbling	No conductivity
	Gas prepared by the wet way	Conductivity
	Rapid reactions, a chemical being put into water	Conductivity
	Gases prepared with the decrepitation of crystals	Conductivity
	Oxidation of sodium in wet air	Weak conductivity
D. Reactions accompanied wth incandescence	Rapid combustion	Conductivity
	Metals in oxygen, chlorine, etc.	Conductivity
	Flames	Conductivity
E. Reactions accompanied with luminescence	Oxidation of phosphorus	Conductivity
	Phosphorescence of sulphur and arsenic	No conductivity
	Phosphorescence of sulphate of quinine	Conductivity

warming gently substances like calcium acetate, lead oxide, carbonate of lead, and oxide of mercury, the finely divided particles given off are neutral. It is true that silver oxide gives off charged particles, but these are probably from the silver atoms.

B. Concentrated nitric acid in contact with benzene, the essence of turpentine, etc., produces a very violent reaction accompanied with the evolution of gas which is neutral, thus showing that in the case of a liquid that does not produce ionization by bubbling, there is no ionization in the gases evolved from at least some chemical reactions.

The formation of ozone by the oxidation of phosphorus seems to be closely related to its ionization and phosphorescence, although the ozone[1] can be absorbed without removing the ionization. The phosphorescence can be removed several meters from the phosphorus, according to Bloch.[2] The oxidation of phosphorus to phosphoric anhydride is without ionization; the oxidation of the anhydride is accompanied by intense ionization. Sulphur at 200° shows phosphorescence and liberates ozone even without ionization. Flames of the thiosulfocarbonic ester, $H_3CSCSOCH_3$, sulfocarbamic ester, $H_3COCSN(CH_3)_2$, and sulfocarbonic ester, $CS(OCH_3)_2$, burn without any accompanying ionization.

Ions of Small Mobility

The ions produced by most of the ionizing radiations possess mobilities of about a centimeter per second, the negative ions usually having a slightly greater mobility. These ions are usually considered as consisting of aggregates (the size depending upon conditions) of gaseous molecules, to or from which one or more electrons have been added or removed. It may be that the ionizing radiation has broken some of the molecules into charged ions, and around these, as nuclei, a cluster of molecules has formed. One might call the ions having a mobility of about 1 cm. per second, small ions. It is these ions that are produced by α-, β-, γ- and X-rays, in the photoelectric effect, by cathode rays, canal rays, etc.

There are other examples of gaseous conductivity, however, in which the ions produced have much smaller mobilities. Bloch[3] has measured the mobility of ions produced when hydrogen is generated by the action of hydrochloric acid on zinc, when carbonic acid gas is made by treating marble with hydrochloric acid, and when oxygen is prepared by heating potassium permanganate. The mobility was found to be about 0.001 cm. per second.

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[1] Physik. Z., **4**, 102 (1903).

[2] Ann. chim. phys., **22** (Apr., 1911).

[3] *Ibid.*, **4**, 25 (1905).

The ions present in a gas that has been bubbled through a liquid have mobilities ranging from those of small ions to those of large ions. The mobility of the ions has a mean value that depends on the nature of the liquid. For pure water the mobilities of both ions are about 0.2 cm. In passing gradually from water to pure sulphuric acid the mobilities of the ions decrease gradually to about 0.0002 cm., this being the mobility of the large ions.

The electrification produced by spraying seems to be produced in the same manner as that by bubbling. The electrification produced by gases prepared by the wet way is due to the presence of charged and neutral centers that seem to be formed in exactly the same way as ions and neutral centers are formed by bubbling. Chemical reactions that take place in the dry way are not accompanied by ionization.

When dust-free air is acted upon by ultraviolet light, Sachs[1] finds ions of small mobility. Air, carbon dioxide, oxygen and nitrogen are found to contain uncharged nuclei.

The most generally accepted hypothesis is to attribute to each ion the same electric charge, and consider the differences of the mobilities to be due to differences in the masses of the material centers. In order to determine the dimensions of these ions, one usually makes use of the law of Stokes: where a is the radius of the particle falling through a medium of viscosity, μ, d is the density of the medium, D the density of the falling particle, v its velocity, and g the value of gravity,

$$4/3\pi a^3 g(D - d) = 6\pi a v \mu.$$

This formula, according to the results of Perrin, seems to hold for particles, the radius of which is as small as 0.1μ. Letting the density be unity, then ions having a mobility of about 0.001 cm. would have a diameter of about $10\mu\mu$. This value is of about the same order as that found by other methods. The limiting thickness, for instance, of a film of oil on water, according to Rayleigh, Schuke, Röntgen, and Fisher, is of the order of several $\mu\mu$. The same bulk is found for solid pellicules which form on the surfaces of liquids (Melsens, Ramsden, Devaux, Metcalf) and for the walls of soap bubbles according to Bleateau, Drude, Reinold and Rucher. The thickness of the black spot of liquid films, which is the smallest thickness that is allowed by the cohesion of the membrane, and which seems to consist of two superficial layers and a central portion, is several $\mu\mu$. Beyond this limit of thickness the ordinary properties of matter would disappear. The molecular diameter is about $0.1\mu\mu$. It would follow then that the smallest drops would contain about 10^6 molecules. Particles of a similar nature are formed when air is passed over phosphorus, in the cooled gases about flames, or in bubbling and the breaking of drops (*ecrasement*), etc. The ions are probably produced by chemical action in the first case, and in the other cases they may be formed at the expense of electrolytic ions, or from the formation of the double layer.

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[1] Ann. Physik, **34**, 469 (1911).

The Charging of Neutral Centers and Their Properties

There are many conditions in which one can imagine the existence of small neutral particles, relatively large compared with molecules and small ions. These centers will attract the ions, and will combine with them to form large ions. Suppose that a gas contains M neutral centers per cc. (the ions having been removed by passing the gas through a charged condenser), and that it is then subjected to an ionizing radiation that will produce p positive and n negative small ions per cc. When equilibrium is reached (which may require a considerable length of time) let there be P positive and N negative "large" ions per cc. When there is equilibrium, it will be supposed that the number of recombinations of neutral centers and of small ions is the same as the rate of disappearance of large ions (dP/dt).

$$dP = A[M - (P + N)]p \qquad (1)$$

A is the coefficient of recombination of the small positive ions and the neutral centers, the rate of recombination being assumed to be proportional to the product of the numbers present. A will depend on the mobilities of the neutral centers and small positive ions. Equation (1) gives the increase of (P). The decrease of P is due to a recombination of large positive ions and large negative ions, and of large positive ions and small negative ions and is:

$$dP = \alpha PN + BPn \qquad (2)$$

For equilibrium,

$$A[M - (P + N)]p = \alpha PN + BPn \qquad (3)$$

Here α, the coefficient of recombination of large ions, will be very small compared with B, the coefficient of recombination of large and small ions. If we asssme that the coefficient of recombination is proportional to the sum of the mobilities of the two kinds of ions considered, then we may neglect the term αPN in Equation (3), especially as n is quite large.

For positive ions, then,

$$M - (P + N) = BP/A \qquad (4)$$

For negative ions,

$$M - (P + N) = B'N/A' \qquad (5)$$

These equations are independent of p and n, showing that the number of large ions is independent of the ionizing radiation if this is of sufficient intensity and depends only on the number of neutral centers present, and certain constants. P/M and N/M are functions of A, A', B, and B', which are in turn functions of the mobilities, and they have a value of about 0.1.

Subtracting (4) from (5), $P/N = AB'/A'B$.

If k_+ or A is the mobility of the small positive ions,

k_- or A' is the mobility of the small negative ions,

K is the mobility of the large ions, then $B = K + k_-$ and $B' = K + k_+$

$P/N = AB'/A'B = k_+(K + k_+)/k_-(K + k_-) = k_+^2/k_-^2$ approximately. Since k_- is greater than k_+, there should be a considerable excess of large negative ions over large positive ions.

Quite an extended investigation has been made by Broglie[1] upon ions of small mobility produced in various ways. To obtain the ions produced by chemical action he passed a mixture of carefully purified air and a small amount of hydrogen through a heated glazed tube, and then into his cylindrical condenser used for measuring the mobilities. (The water formed in this way indicated the presence of hydrogen dioxide.) Currents of hydrogen mixed with small quantities of air have given exactly analogous results. (Currents of hydrogen passed through copper oxide did not show any ionization, but this may have been due to loss of the ions by diffusion.) The intensity of the ionization depended very much upon the way the tube in which the chemical reaction took place was heated. The mobility of the ions is much less than that of the small ions, but greater than that of the ions from flames. The mobility is found to decrease as the proportion of hydrogen is increased, and may be explained by supposing that the neutral centers are larger, the greater the amount of water condensed.

In the case of a chemical reaction in which there is no condensation, as in a carbon monoxide flame, no neutral centers would be formed, and therefore no large ions. Broglie has found that the mobility of ions from such a flame was about 0.05 cm. and was independent of the proportion of carbon monoxide. When the heated tube through which the air and carbon monoxide flow is free from any volatile substances, and the gases are thoroughly dry, there is no indication of a stable conductivity. Even in the case of a flame of carbon monoxide there is no indication of any conductivity when the entering gases are carefully purified.

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[1] Ann. chim. phys., **16**, 1–69 (1909).

If, however, the air admitted contains a little moisture, or the carbon monoxide a small amount of hydrogen, there is a large conductivity due to the presence of large ions. By heating a moist porous body at varying distances from the carbon monoxide flame, it is found that large ions are produced only when the source of neutral centers is close to the flame, thus indicating that in the flame there are produced small ions that possess a very large coefficient of recombination, similar to those produced by X-rays given off by radium.

It is possible to produce large ions in moist filtered air without any ionizing agent by passing it through a porcelain tube containing pumice stone heated to a dull redness. In this case the large ions are probably due to the dissociation of the water vapor.

In the formation of large ions in the cases above cited, it seems necessary to have present neutral centers; and these neutral centers are not always present in a gas containing water vapor. Broglie has shown this by warming a flask containing water and exposed to a tube of radium. Large ions are not produced in a gas made to pass through the flask of water until all the water has evaporated, and the flask is heated to 200° or 300°.

Broglie has found that neutral centers are easily filtered from a gas by passing the gas through cotton. They are destroyed when the gas is heated to a temperature greater than 250°. When a gas is removed from a flame, the number of ions gradually decreases. At the same time, the number of neutral centers also decreases, and apparently at about the same rate as the large ions. The proportion of large ions to neutral centers, $(P + N)/M$, is very small.

In 1894 Lord Kelvin[1] showed that air bubbled through water was charged negatively. This charge was decreased when salts or acids were added to the water, and in some cases the ionization of the air was reversed. In 1894, Thomson[2] showed that the presence of infinitesimal amounts of impurities in the water (such as rosaniline, for example) had a very great effect upon the ionization.

Kösters,[3] in 1900, showed that when 0.007 part of sulphuric acid per 100 of water was used, the air that bubbled through the solution was neutral. If the amount of acid was greater, the air was positive; if less, the air was negatively charged.

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[1] P. Roy. Soc., **57**, 335 (1894).

[2] Phil. Mag., **37**, 341 (1894).

[3] Ann. Physik, **59**, 12 (1899).

Lenard,[1] having his attention drawn to the exceptional atmospheric electrical phenomena about waterfalls, examined the effect of water splashing against a plate, and found that the water becomes positively charged and the surrounding air negatively charged. He found the effect to depend largely on the purity of the water, and in the case of a weak solution of sodium chloride, he noticed that the air was positively electrified. Lenard shook mercury in a bottle, and found the air negatively charged. Turpentine, in being sprayed, became negatively electrified and made the air positive, the effect being the opposite of that of water. Carbon bisulphide gave the same effect as water. In the case of water, the presence of hydrogen caused the amount of electrification to be much smaller. Kähler's[2] work indicates that in bubbling through pure water, only negative ions are formed in the air, whereas when salts are present both kinds of ions are formed. Aselmann[3] finds that the mobility of ions in air made by splashing pure water varies from 4 cm./sec. to 0.00027 cm. per second, the mobility of the greater number of ions being from 4 cm. to 0.016 cm. per second. For a 0.2 per cent. solution of sodium chloride, the mobilities of the negative ions ranged between 4 cm. to 0.0019 cm. per second, while the mobilities of the positive ions were between 0.088 and 0.0006 cm. per second. Pacini[4] has studied the ionization produced by bubbling in water containing a trace of coloring matter. Solutions containing eosin, resorcinol, etc., communicate to a gas a charge that is independent of the concentration, whereas rosaniline, fuchsine, etc., produce an ionization whose sign is variable. Bloch[5] gives the mobility of the negative ion produced in air bubbled through pure water as 0.115 cm. per second, and 0.08 cm. per second for the positive ion. For sulphuric acid, the mobility is about 0.0003 cm. per second. A thorough investigation has been made by Broglie,[6] and some of his results will now be given.

The phenomena are very complex, the ionization in the gas depending upon the chemical nature and condition of the gas, the nature and temperature of the liquid, the form of the orifice from which the bubbles are produced, the distance of the orifice below the surface of the liquid, and the amount of pressure under which the gas issues from the orifice.

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[1] Ann. Physik, **1892**, 584.

[2] *Ibid.*, **12**, 1119 (1903).

[3] *Ibid.*, **9**, 960 (1905).

[4] Atti accad. Lincei, **1904**.

[5] Compt. rend., July 1, **1907**.

[6] Ann. chim. phys., **16**, 42 (1909).

As the pressure of the gas is increased at the orifice where the bubbles are formed, the intensity of the ionization is very small until the pressure reaches about 9 cm. of mercury, and then it rises very rapidly and is approximately proportional to the pressure. Using the same size of orifice, the intensity of ionization is much greater for an alcoholic solution. Increasing the size of orifice from 0.15 mm. to 0.35 mm. also increases the ionization.

Starting with pure water, the ionization is measured for solutions containing varying amounts of a large number of salts and acids (sodium, potassium and barium chlorides, potassium bromide and iodide, hydrochloric, sulphuric and acetic acids, potassium hydroxide). Curves are plotted between the intensity of (positive) ionization and concentration. The ionization, small at first, in general rises rapidly to a maximum at about 0.0015 normal, and then decreases slowly. The curve for the negative ions starts with a considerable value, attains a maximum for a concentration of about 0.005, and then descends. It cuts the curve for the positive ions at about 0.01 normal concentration, remains for a long distance in the same region, and then falls for the strong concentrations. The total charge would be represented by a difference in the ordinates of the two curves. As the form of the curve does not vary when the bubbling is done at different depths in the liquid, it would seem that recombination does not influence the results.

The curve representing the ionization resulting from a solution of alcohol or ether in water is very different from the effect produced by the addition of a salt. An example is the following:

KCl in water	Conductivity	Alcohol in water	Conductivity
0	100	0	100
N/152000	134	N/152000	104
N/38500	229	N/38500	113
N/4000	422	N/4000	116

In general, air bubbled through methyl and ethyl alcohols, ether, acetone, aldehyde, pure sulphuric acid and aniline contains ions, while air bubbled through benzene, toluene, xylene, carbon bisulphide, carbon tetrachloride, pentane, hexane, chloroform, the essence of turpentine, liquid air, etc., produces only neutral centers that can be ionized by the rays from radium. The two classes of liquids have very little in common. Broglie believes that there may be some connection between the power of the first group of liquids to absorb oxygen and the electrical effects produced by bubbling. Mercury produces neither ions nor neutral centers, and so does not belong to either of the above classes. The ionizing effect produced when mercury is shaken in a vessel must be of a different nature from that produced by other liquids. Pure glycerol and oil of vaselin give neither ions nor neutral centers.

The phenomena observed when oxygen or hydrogen are used instead of air are essentially the same, although in the case of hydrogen the mobilities of the ions are somewhat greater.

In the case of liquids of the first class, it is found that an exposure to X or radium rays actually reduces the ionization, and in an example given by Broglie this decrease amounted to about 85 per cent.

Bloch[1] finds that if a little olive oil, benzene, petroleum, vaselin, turpentine, etc., is poured over the surface of a liquid in which a gas is being produced by the wet way, no ionization results. This layer of oil can be made very thin if the gas evolved consists of very small bubbles. These results, with the work of others, might then be taken to indicate that the ionization by bubbling, the Lenard effect (ionization due to the falling or splashing of drops), and the ionization produced by chemical reactions, are all due to a common cause. For instance, bubbling is usually, if not always, accompanied by the formation of a fine mist, so that the accompanying ionization may simply be a Lenard effect. This view is supported by the fact that the ionization effect for fine spray of a liquid is the same as that produced by bubbling.

The ions produced by bubbling possess varying mobilities, the ions from sulphuric acid being "large," whereas those formed by the bubbling of pure water are small. The ions produced during chemical reactions also have varying mobilities. Bloch has used the surface of a liquid in which chemical reactions are taking place as one of the plates of a condenser from which he measured the saturation curves. These "static saturation" curves are found to be straight lines that keep on ascending to at least a field strength of 1100, which is as far as Bloch worked. The curves are the same for positive and for negative ions, and are similar to those found by Miss Gates[2] for the ionization from sulphate of quinine.

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[1] Le Radium, **7**, 354 (1910).

[2] Physic. Rev., **18**, 146.

Bloch considers that the curves are due to the production of ions and neutral particles, and that the latter may become charged in an electric field and play a more important role than the ions. In chemical reactions these neutral particles, or liquid dust, often become charged, and they can then be distinguished from ions, since their charges and their mobilities are a function of the electric field in which they are formed. The neutral particles of Bloch are very similar to the neutral centers studied by Broglie and others, although there are some differences. Bloch, for instance, finds the neutral centers in hydrogen do not become charged when exposed to the rays from radium, whereas Broglie finds that under such circumstances the neutral centers become large ions. Broglie finds neutral centers from the bubbling of inactive liquids such as benzene, and does not obtain them for water. Bloch finds them, however, for solutions that are "active," by bubbling. Broglie's neutral centers are visible in the ultramicroscope, whereas those found by Bloch in hydrogen are not, being too small to appear optically.

Charging these neutral particles by the action of an electric field, and letting e', K', D' and r be the charge, the mobility, the coefficient of diffusion and the radius of the ions, we have

$$K'/D' = Ne'$$

$$e' = 6\pi\mu r K' \text{ (Stokes' law)}$$

K' is found to be 0.19 cm. per second. By using Townsend's method,[1] the coefficient of diffusion was found to be $D' = 0.0017$. Using $K = 1.16$, and $D = 0.035$, $e'/e = 2.5$, the value e' being a mean one. Broglie's large ions often have a charge of 30 to $50e$.

Electrolytic oxygen from potassium hydroxide and sulphuric acid solutions contain charged mist nuclei. The charges on these nuclei are e, $2e$ and $4e$, according to Lattey.[2]

Ehrenhaft[3] has investigated, by the ultramicroscopic method, the charge of isolated particles produced by arcs of gold, silver and platinum. The method was to measure the velocity of the fall of the particles in the presence of an electric field, and then in absence of the field. The particles were found to be spherical and metallic, and certainly were of sufficient size for Stokes' law to apply. The work was done in a dry gas for the reason that in the presence of moisture the particles showed a very marked Brownian movement similar to that of particles of phosphorus fumes.

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[1] Conduction of Electricity, p. 420.

[2] Phil. Mag., **18**, 26 (1909).

[3] Physik. Z., **11**, 619 (1910).

For phosphorus, *e* varied from 0.52 to 28.90 × 10^{-10}; for gold, from 0.53 to 7.18 × 10^{-10}; for silver, from 0.94 to 26.65 × 10^{-10}; and for platinum, from 1.5 to 12.43 × 10^{-10}. A large number of measurements led to values much less than the classic value 4 × 10^{-10}. Efforts to find statistical groupings of the value of *e* were unsuccessful, so that it is concluded that there exist electric charges that are much smaller than the charge on the electron.

Humidity influences positive and negative ions in such a way that the negative ions act more easily as nuclei for the condensation of water vapor. It might be expected, therefore, that any damp ionized gas that is dried by being passed through a tube plunged in liquid air would show an excess of positive ions. Lusby[1] does not find this to be the case, although he finds that the dried air possesses from two to three times as many ions. In his experiments, the ionizing agent consisted of uranium oxide. Lusby considers that this effect is not due to diffusion, because it is independent of the size of the tubes; and that it is not due to a variation in the number of large and small ions, because the effect is the same when only small ions are present. Recombination should not produce such an effect, since Erkson has found that the coefficient of recombination increases as the temperature decreases. The large increase in ionization after passing through liquid air is found to occur for dry air, and is therefore not dependent on moisture.

Mme. Curie[2] has shown that the presence of radium emanation causes the condensation of certain vapors in the form of a persistent mist that can be seen in the light of an electric arc. The condensation centers are probably particles of the induced radioactivity that are suspended in the gas and the mist is probably due either to the action of electrostatic attraction or chemical affinity. The radium emanation causes a feeble mist for several days in the presence of pure water and air. In carbon dioxide and water no mist is formed, but if some sulphuric acid is present a mist is formed. The condensation centers in the above cases may be nitrogen compounds and particles of sulphuric anhydride formed during the decay of the radium emanation. Persistent and thick mists are formed with iodine in carbon dioxide, and camphor in air.

Molecular Aggregates Produced in Gases by Sudden Cooling

Owen and Hughes[3] describe experiments that show that certain gases when suddenly cooled contain a large number of charged nuclei which act as centers for the condensation of supersaturated water vapor. The temperature below which it is necessary to cool the gas, in order that these nuclei be formed, is designated as the nucleating temperature. The nucleating temperature is found to depend to some extent upon the rate at which the gas is cooled, and upon the dimensions of the vessel used.

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[1] P. Camb. Phil. Soc., **15**, 459 (1910).

[2] Compt. rend., **147**, 379 (1908).

[3] Phil. Mag., Oct., **1907**, p. 746; June, **1908**. Owen: *Ibid.*, Oct., **1911.**

It was found that many gases differ from air. In air and similar gases, it is possible that aggregations of the slowly moving molecules are formed, a sort of incipient liquefaction. The number of these molecular aggregates, for some unexplained reason, is much larger if the cooling is sudden. The rapid disappearance of the nuclei at higher temperatures is probably due to the more vigorous bombardment by the more rapidly moving gas molecules.

Air containing these nuclei, when left to stand for twenty or thirty minutes, is found to be practically free of them. For dusty air, however, these nuclei are much more persistent, as they also are at low temperatures.

No nuclei are formed in carbon dioxide, ethylene, methane, etc., by cooling until the temperature of condensation is reached. When condensed carbon dioxide is allowed to sublime, nuclei are formed, indicating that aggregates as well as separate molecules escape; on the other hand, the gases from liquid air, oxygen, ethylene and methane are free of nuclei, indicating that the evaporation of a liquid consists in the escape of separate molecules.

C. Barus[1] and Owen and Pealing[2] have not obtained any evidence for the existence of nuclei in air blown over camphor, naphthalene or benzoic acid. Owen and Pealing obtained quite marked effects, however, with iodine in moist air and oxygen. They found that the effects are very persistent, and are only produced by the action of light. The nuclei seem to be quite small, and apparently grow to their maximum size after the light has acted for about a second. The nuclei all disappear about a minute after the light has been screened off.

The iodine nuclei are uncharged, and are only effective when the expansions take place in supersaturated water vapor in the presence of light. The effect seems to be photochemical in character, and probably belongs to the class of phenomena studied by Tyndall,[3] Aitken[4] and C. T. R. Wilson.[5] Tyndall found that ultraviolet light caused clouds to form without expansion in air containing traces of amyl nitrite, iodide of allyl and other vapors. Aitken found that clouds are produced in ammonia, sulphurous acid, hydrogen sulphide, hydrochloric acid and chlorine, when expanded after exposure to sunlight. Wilson found that moist air or oxygen, when exposed to intense ultraviolet light, produced condensation nuclei on which clouds could be obtained without any expansion at all. Wilson has suggested that this cloud formation is due to the formation of hydrogen peroxide. Bevan,[1] in his experiments on the combination of hydrogen and chlorine under the influence of light, found that some substance is produced by the action of light on chlorine and water vapor that acts like condensation nuclei, and that the formation of these nuclei is necessary for the production of hydrochloric acid.

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[1] "Condensation of Vapor as Induced by Nuclei and Ions," Carnegie Institution of Washington, May, 1907.

[2] Phil. Mag., **21**, 466 (1911).

[3] Phil. Trans., **160**, 333 (1870).

[4] P. Roy. Soc. Edinb., **39**, 15 (1897).

[5] Phil. Trans., **192**, 403 (1899).

The iodine nuclei are not produced after the iodine has been in the apparatus for a few days, but reappears as soon as the glass walls of the apparatus are rinsed with water. The passage of the iodine vapor facilitates the formation of the nuclei very greatly.

In experiments upon condensation nuclei it is very important to eliminate the effect of impurities. Lenard[2] and Wolf showed that the uncharged nuclei are often present in a gas and that these are copiously formed by the action of ultraviolet light. These nuclei are unaffected by cooling but are destroyed when heated to about 180°. Their diameter appears to be twenty or thirty times that of gas molecules and they are probably products of chemical reactions.

Ionization in Sprays

Allesandrini,[3] Wilson,[4] Eve,[5] Pomeroy,[6] and many others have studied the ionization produced by the fine spray of water. The relative number of negative to positive ions was found by Eve to be in the ratio of 4 to 3. Both positive and negative ions are removed by filters of glass wool (6.5 cm. thick). Such a filter can be used as a "Faraday box" to measure the total charge carried off by the air or spray. By this means it can be shown that a current of air and spray contains an excess of negative electrification. The heavier part of the spray that falls is charged positively. It also seems probable that most of the positive ions become attached to water drops while the negative ions do not seem to become so

[1] Phil. Trans., **202**, 347 (1903).

[2] Ann. chim. phys., **3**, (1889); Ann. Physik, **1900**, Nos. 1 and 2.

[3] Nuovo Cimento, **4**, 389 (1902).

[4] Phil. Mag., July, 1902.

[5] *Ibid.*, **1907**, 382.

[6] Physic. Rev., **27**, 492 (1908).

easily attached. Evaporation does not seem to be accompanied by ionization, although, according to Holmgren,[1] ripples on a water surface produce ionization. Interesting experiments could be carried out by electrifying the nozzle and in passing the spray through various kinds of electrical discharges.

Lousdale[2] finds that the splashing of mercury on an iron plate produces a large excess of positive ions, and that a considerable portion of these ions have a small mobility. The amount of ionization depends upon the nature of the surface upon which the mercury is splashed. Becker[3] has measured the mobility of the ions produced by the fall of mercury in hydrogen and carbon dioxide, the mercury drops striking a solid obstacle. He finds that there is no definite value, but that there are ions of all mobilities. Immediately after their formation, the mobilities range between 0.96 and 0.015 cm. per second. After a short time large ions of a mobility of from 0.0062 to 0.0027 appear, and the number of these large ions continues to increase.

If a stream of water is directed vertically to a distance of several feet and then allowed to fall on a sheet of metal, the sound of the falling drops will be heard.[4] Bringing a charged body near the jet, where it breaks into drops, will result in the formation of larger drops and hence a sound of lower frequency. When the stream is small the drops are found to form in a line when charged, but scatter when uncharged, and it appears to be due to this fact that the charged drops tend to coalesce more as they go upwards. These phenomena hold only when the drops carry small charges. The coalescence of the charged drops is probably due to their being of quite different sizes.

The action between two spheres[5] charged with the same sign of electricity is not always one of repulsion. The force will be one of attraction in many cases, as shown by Burton and Wiegand, and this probably explains the coalescence of the charged drops. This attraction, combined with the Bjerknes effect, may play a considerable role in the aggregation of particles suspended in gases.

Seeliger[6] finds that falling water drops carry down but a small negative charge when they pass through air that is being ionized by X-rays. Great care must be taken to eliminate the "water-dropper" effect of the drops leaving the nozzle and the Lenard effect. The charge carried down by the drops is measurable only when the X-rays are acting. This is probably due to the air film about the drop being more strongly ionized, owing to secondary radiation from the drop.

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[1] Soc. Physiographique de London, **1894**.

[2] Phil Mag., **20**, 464 (1910).

[3] Ann. Physik, **31**, 98 (1910).

[4] See various sections of Lord Rayleigh's papers. Burton and Wiegand: Phil. Mag., **23**, 148 (1912).

[5] Collected papers of Lord Kelvin. Russel: Physic. Soc. London, **24**, 22 (1911).

[6] Ann. Physik, **31**, 500 (1910).

The Production of Nuclei

H. A. Wilson and others have shown that X- and γ-rays not only produce ions in a gas, but nuclei also. These nuclei can be detected in the production of a sudden expansion of the gas, by decreasing the pressure (δp), so that there is a supersaturation of the water vapor present; and if the expansion is sufficient, condensation of water vapor follows. Barus defines the fog limit as the amount of expansion (δp) necessary to cause dust-free air saturated with water vapor to condense so as to form clouds. A very extended study has been made by Barus[1] upon the coronas that are produced by fogs and clouds when a beam of light passes through them.

When nucleation and ionization are produced by the same process, the intensity of the two phenomena remains relatively about the same, both nuclei and ions being produced at the same rate. The subsequent life history of nuclei and ions, however, is quite different, nuclei being in general very fleeting. In some cases nucleation may be a result of ionization, though many cases are known of nucleation without any accompanying ionization.

The apparatus of Barus usually consisted of a long rectangular wooden condensation chamber having plate glass windows. A layer of water is kept in the bottom to keep the air saturated with water vapor. One end of the apparatus is exposed to an X-ray bulb and the other end is connected with an apparatus for producing sudden exhaustion.

A pressure difference is selected such that condensation just begins for dust-free air; and for the apparatus used the volume expansion was about 1.48. The number of nuclei range from 11,000 to 95,000 per cc. for dust-free filtered air. According to Barus, dust-free air contains large and small nuclei to the number of millions per cc., and these rapidly increase as the order of molecular size is approached. These nuclei Barus considers as a kind of colloidal air molecule.

While the phosphorescent, photographic and ionizing effects of an X-ray bulb decrease rapidly with the distance, the nucleating effect is nearly constant, according to Barus, over distances in some cases varying from six to six hundred cm., and the nucleating radiation is not stopped by lead screens several cm. thick when the fog chamber is not protected. When the fog chamber is surrounded with lead, and only a small window is left open, the nucleating power of the rays acts in the same manner as the ionizing power. When the nucleating effect is almost independent of the distance, it is probable that the effect is due to secondary X-rays.

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[1] Carl Barus: Smithsonian Contributions, Nos. 1373, 1903, Vol. 34, 1905. Science; Apr. 14, 1905. Publications Nos. 40 and 62, Carnegie Institution of Washington, etc.

There are several kinds of nuclei present in dust-free air. These Barus classifies as persistent, fleeting, and colloidal nuclei.

Ordinary dustlike or persistent nuclei can be separated from air by passing it through a cotton filter. These nuclei require the smallest amount of supersaturation of water vapor to produce condensation. As a rule, they consist of foreign bodies in the air, although they can be produced by X- and γ-rays that are of sufficient intensity. This kind of nuclei may persist for hours after the exciting radiation is removed, decaying to half value in ten minutes, and one-fifth value in eighty minutes. Their number keeps increasing for ten minutes or more after the exciting radiation is turned on.

Intermediate rates of generation and decay may be obtained by having the X-ray bulb of radium at varying distances from the fog chamber.

The second kind of nuclei vanish in a few seconds after the exciting radiation is removed. These are named fleeting nuclei, and for the production of corona they require an exhaustion almost approaching the value of the fog limit. They seem to be almost instantaneously generated—at least, in less than a second's time—by the radiation that produced them. On the removal of the radiation, they decay according to an exponential law, their number falling to half value in two seconds, and to one-fifth value in twenty seconds. If charged, these nuclei seem to be the ordinary ions. Their size seems to depend upon the kind of radiation by which they are produced. Fleeting nuclei pass continuously into persistent nuclei. When condensation takes place upon fleeting nuclei, about one-fourth of these nuclei become persistent nuclei upon the re-evaporation of the clouds formed. Barus thinks that all nuclei upon which there has been condensation become stable and persistent. These nuclei may be called solutional nuclei. If N is the number of these nuclei per unit volume and the source of nuclei is cut off the number of nuclei decrease so that

$$dN/dt = -\alpha N^2$$

where $\alpha = 0.002$.

According to Barus, colloidal nuclei are a structural part of a gas, and are always present. They are reproduced as rapidly as they are removed. Their number increases rapidly as their diameter decreases to that of molecular dimensions. Barus considers that the size of molecules varies in somewhat the same manner as the velocity is distributed amongst them. The number of colloidal nuclei is much greater than the number of ions, and increases rapidly as the size of the nuclei becomes smaller. Barus considers that the action of an external radiation or of an expansion is to cause a sort of flocculation of the colloidal nuclei. The presence of strong odors (camphor, naphthalene, turpentine, etc.) did not have any apparent effect in nucleation. (The exact nature of these odors does not seem, therefore, to be that of colloidal nuclei.) No diurnal variation was observed in the number of colloidal nuclei.

Barus[1] has done a little work on exhaustions in other gases than air, and also by using liquids other than water. He has found the number of nuclei to vary with the solvent, and with the solute dissolved in it. Thus he finds, for shaking, the value of N (number of nuclei per cc.) for pure water, 130; organic substances dissolved in water (sucrose, glucose, glycerol, urea, etc., 1 per cent. solution), $N = 600$; mineral salts dissolved in water (1 per cent. solution) (nitrates, chlorides, sulphates, etc.), $N = 1300$; naphthalene in benzene, $N = 3500$; paraffin in benzene, $N = 5000$. If the solvent is pure, the nuclei produced by shaking are very fleeting, and as the concentration increases for a given solvent, the persistence increases with the number of nuclei formed.

Positive Rays

Some very important discoveries have been made by J. J. Thomson on the value of the charge and the mass of ions in the "positive" rays of vacuum tubes. The measurements simply consist in obtaining the deflection of the rays by the action of magnetic and electric fields. In the positive rays ions of the following type have been found: $\overset{+}{\mathrm{H}}_2$; $\overset{+}{\mathrm{H}}$; $\overset{-}{\mathrm{H}}$; $\overset{-}{\mathrm{O}}_2$; $\overset{-}{\mathrm{O}}$; $\overset{+}{\mathrm{C}}$; $\overset{+}{\mathrm{CH}}_4$; $\overset{-}{\mathrm{CN}}$; $\overset{+}{\mathrm{He}}$; $\overset{-}{\mathrm{Cl}}$; $\overset{+}{\mathrm{H}}_3$; $\overset{++}{\mathrm{He}}$; $\overset{++}{\mathrm{C}}$; $\overset{++}{\mathrm{N}}$; $\overset{+}{\mathrm{He}}_3$; $\overset{+}{\mathrm{O}}$; $\overset{+}{\mathrm{CN}}$; $\overset{+}{\mathrm{C}}_3$; $\overset{+}{\mathrm{O}}_3$; $\overset{+}{\mathrm{C}}_6$(?); $\overset{+}{\mathrm{O}}_6$; $\overset{++}{\mathrm{Hg}}$; $\overset{+}{\mathrm{Hg}}$; $\overset{+}{\mathrm{Hg}}_4$; $\overset{++}{\mathrm{O}}$; $\overset{+}{\mathrm{N}}$; $\overset{+}{\mathrm{N}}_2$; $\overset{+++}{\mathrm{N}}$; $\overset{+++++}{\mathrm{Kr}}$; $\overset{++++}{\mathrm{N}}$; $\overset{+}{\mathrm{Ar}}$; $\overset{++}{\mathrm{Ar}}$; $\overset{+++}{\mathrm{Ar}}$; $\overset{-}{\mathrm{C}}$; $\overset{-}{\mathrm{S}}$; $\overset{-}{\mathrm{Cl}}$, etc. This method has proven valuable in analyzing small quantities of gas and by its use Thomson believes that he has discovered several new elements.

Up to the present time the method has not been applied to the determination of the exact nature of chemical reactions.

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[1] Am. J. Sci., **33**, 107 (1912).

One of the difficulties of an application is the temporary nature of many of the ions of any given kind of ray. The method does permit a beam of a certain kind of ions being sorted from the main beam of positive rays so that it would seem possible to throw a beam of $\overset{+++}{N}$, for instance, against tungsten. It might also be possible to focus a beam of $\overset{+}{N_2}$ on another beam of $\overset{-}{O}$; or a beam of $\overset{+++}{N}$ on a beam of $\overset{-}{O_6}$ and observe what takes place.

The Dissociation of Molecules of Moving Ions and the Dynamics of Chemical Reactions in Gases

According to Kirkby,[1] an electron is not only able to break up molecules into charged ions by collision, but it can break up a molecule like oxygen into its component atoms. The ionization of a molecule like oxygen requires much more energy than the breaking up of a molecule into neutral parts, and may be presumed to occur only when the velocity of the electron is sufficiently great. Positive ions may also have the power of dissociating molecules, and of bringing a gas into the active state, so that it can form new combinations. The experimental results of Kirkby lead to the conclusion that atoms of oxygen, when separated, are not charged electrically, so that there must be other than electrical forces that bind the atoms in the molecule together.

Kirkby has found that when a steady discharge passes through an electrolytic gas at a pressure p mm., the number of molecules of water vapor formed by the passage of an atomic charge through 1 cm. of the positive column where the electric force is E_x is $7.9\, pe - 42.7\, p/E_x$. The chemical effects in the positive column are due to the collisions of the electrons dissociating the oxygen molecules into atoms and under these conditions the oxygen atoms, when they collide with hydrogen molecules, unite with them to form water molecules.

In Kirkby's experiments, only about half of the collisions between electrons and oxygen molecules resulted in the formation of oxygen atoms. The energy of the formation of an oxygen molecule is given as 5.3×10^{-12} ergs, and of a molecule of water vapor as 6.4×10^{-12} ergs.

The collision constants[2] seem to be independent of the ionizing agent, as would be expected. The general theory of ionization by collision has also been found to apply to vapors as well as to gases if the pressure is not too high.

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[1] P. Roy. Soc., A, **85**, 171 (1911).

[2] Barus: Am. J. Sci., **34**, 229 (1912).

At high temperatures the power consumption necessary to maintain a tungsten wire at a given temperature increases with abnormal rapidity with the temperature. Langmuir[1] considers that this energy is absorbed by the dissociating hydrogen gas near the wire, the hydrogen atoms again recombining after they diffuse some distance from the wire. The effect begins at 2100° C. (abs.) and the heat of the reaction is given at 130,000 calories.

Langmuir[2] considers that the oxidation of tungsten in an incandescent lamp bulb is not due to a direct reaction between the oxygen molecules and the tungsten atoms, but that the oxygen atoms must first become negatively charged by collision with electrons. Only electrons with a velocity exceeding 6×10^{-7} cm. per second are considered as being able to charge oxygen atoms. In a reaction of this type the velocity of the oxygen atoms is affected but little with rise in temperature of the tungsten filament so that the number of variables entering into the reaction can be considerably reduced.

It seems, therefore, that once the oxygen molecule is charged negatively, it can be held by the positively charged tungsten atoms and "secondary reactions" then take place, resulting in the formation of the oxide WO_3. The ratio between the number of oxygen molecules colliding with the tungsten filament and those combining with the tungsten to form the oxide WO_3 for the various temperatures of the filament is as follows:

Temperature (absolute)	Ratio observed	Ratio calculated
1070	0.00033	0.00016
1270	0.0011	0.0012
1470	0.0053	0.0052
1770	0.0255	0.0256
2020	0.049	0.066
2290	0.095	0.145
2520	0.12	0.26
2770	0.15	0.42

The calculated value based on the assumption that electrons are emitted by the tungsten with a Maxwell distribution of velocity and that the oxygen molecule unites with an electron exceeds that given above. W. W. STRONG

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[1] J. Am. Chem. Soc., **34**, 260 (1912).

[2] *Ibid.*, **35**, 126 (1913).

REVIEWS

Traité de Chimie Minérale. Par H. Erdman, Directeur de l'Institut de Chimie Minérale de la Technische Hochschule de Berlin. Ouvrage traduit sur la 5e Édition allemande par A. Corvisy, Professeur Aggrégé des Sciences Physiques au Lycée Gay-Lussac, Professuer Suppléant à l'Ecole de Médecine et de Pharmacie de Limoges. Tome Premier. Introduction à la Chimie et Métalloides. Avec 243 figures et 2 planches spectrales coloriées. Paris: Librairie Scientifique A. Hermann et Fils. 1913. pp. iv + 559. Price, Fr. 12.00.

French chemists are to be congratulated upon now having at their disposal this translation of Erdmann's well-known book. The ability of Prof. Corvisy as a translator has already been shown in the French versions prepared by him of Ladenburg's "History" and "Nernst's Theoretical Chemistry." The type and illustrations in the present volume are clear, the paper good. C. A. R.

Les Nouveautés Chimiques pour 1913. Nouveaux Appareils de Laboratoires, Méthodes Nouvelles de Recherches Appliquées à la Science et à l'Industrie. Par Camille Poulenc, Docteur es Sciences. Avec 195 Figures intercalées dans le Texte. Paris: J. B. Baillière et Fils. 1913. pp. viii + 329. Price, Fr. 4.00.

The present volume, the eighteenth of this useful annual, is, as usual, divided into five chapters under the following headings and subheadings: I. General Applications of Physics to Chemistry (63 pp.): Determination of Densities; Determination of Temperatures; Determination of Melting Points; Calorimetry; Microscopy; Colorimetry; Spectroscopy. II. Miscellaneous Laboratory Apparatus (65 pp.): Heating Apparatus; Distillation Apparatus; Extraction Apparatus; Apparatus for the Production of Gases; Apparatus for Producing a Vacuum or Compressed Air; Filtration Apparatus; Miscellaneous Apparatus. III. Electricity (16 pp.): Heating Apparatus; Miscellaneous Apparatus. IV. Chemical Analysis (141 pp.); General Analytical Apparatus, Burettes, Pipettes, etc.; Miscellaneous Apparatus; Industrial Analyses, Gas Analyses, Miscellaneous Analyses, Apparatus for the Detection or Separation of Arsenic, Metallurgy, Analyses of Alimentary Substances, Medical Analyses. V. Bacteriology (25 pp.); Apparatus for Sterilization or Cultures; Apparatus for Keeping or for Taking Samples for Bacteriological Investigation; Miscellaneous Apparatus.

The book is well worth looking through. C. A. R.

Chemical Theory and Calculations. An Elementary Text-Book. By Forsyth James Wilson, D.Sc. (Edin.), Ph.D. (Leipzig), and Isidor M. Heilbron, Ph.D. (Leipzig), F.I.C., A.R.T.C., Lecturer in

Chemistry, the Royal Technical College, Glasgow. New York: D. Van Nostrand Co. 1912. pp. 138. Price, $1.00.

This little book is divided into twenty-one chapters, which cover pretty thoroughly all phases of elementary chemistry involving arithmetical operations, beginning with "The Metric System" and ending with "Thermochemistry" and including such subjects as "Valency" and "The Periodic Classification of the Elements," which are not usually included in "chemical arithmetics." In each chapter the theory of the subject dealt with is briefly developed and numerous problems of a practical nature are given. The treatment throughout seems to be quite clear. C. A. R.

WHO'S WHO IN SCIENCE, INTERNATIONAL, 1913. Edited by H. H. STEPHENSON. London: J. and A. Churchhill. pp. xvi + 569. Price, $3.50.

New features in this issue of the international "Who's Who in Science," are a section on "The World's Societies" (including name, address, president and secretary, date of foundation, number of members, annual subscription and periodical publications) and a frontispiece consisting of portraits of prominent scientists who have died in the preceding year (van't Hoff, Hooker, Lister, Poincaré, Strassburger). Psychology and Geography have been added to the sciences represented. Besides these, the book contains an "Obituary for 1912;" a section on "The World's Universities," giving the site, date of foundation, president, registrar and senior professors of the different departments; "Biographies;" and a "Classified Index" in which the names of the men whose biographies are given are grouped under subjects and these groups again subdivided into nationalities. Great Britain is naturally better represented than other countries; thus, under "Chemistry, Pure and Applied," we find the names of 126 German, 281 British, 228 American and only 42 French and 12 Italian chemists. C. A. R.

FORTSCHRITTE UND PROBLEME DER CHEMISCHEN INDUSTRIE. Vortrag, gehalten in der allgemeinen Sitzung des VIII Internationalen Kongresses für Angewandte Chemie am 9 September, 1912, in New York. Von C. DUISBERG. Leipzig: Verlag von Otto Spamer. 1913. p. 32.

A debt of thanks is due to the publishers for making available, in such convenient form, this interesting and authoritative, though necessarily brief, review of the most recent advances made and the more important problems now being studied in the field of industrial chemistry. C. A. R.

EVANS' ANALYTICAL NOTES FOR 1912. From the Laboratories of EVANS' SONS, LESCHER AND WEBB, Limited, Wholesale and Export Druggists and Manufacturing Chemists, Liverpool and London. No. 7. 92 William St., New York. March, 1913. pp. 100.

The following words are taken from the preface: "...... the researches of science are being employed in an illegitimate as well as in a legitimate direction to help the manufacturer. ...... During the years under review (1912) upwards of 10,000 samples have passed through the hands of our Analytical Laboratory, and the notes now presented form a *precis* of the more interesting examinations made and the researches undertaken by our chief chemist, Mr. H. R. Jensen, B.Sc., and his assistants. The necessity for analytical control in all directions is made obvious by the fact that of the 2,400 samples herein referred to, 250 were reported upon as falling below the standard. It must also be borne in mind that such control tends to raise the standard of samples submitted to us.

"Tables dealing with melting points, volumetric equivalents, resin constants and impurity limits have been carefully compiled, and together with the oil tables, which have been revised up to date, form an appendix to the notes." C. A. R.

REPORT OF LEHN AND FINK'S ANALYTICAL DEPARTMENT FOR 1910–1912. By HORACE NORTH, assisted by F. H. SCHORTEMEYER. New York: Lehn & Fink, Wholesale Druggists and Manufacturing Chemists. January, 1913. pp. 98.

Lehn and Fisk take a more optimistic view of the state of the drug industry than the English firm whose analytical report is noticed above. They say: "Some of the more interesting work of the past three years is reviewed in the following pages. While the notes are somewhat discursive, it is believed that they will, in many cases, prove suggestive. Data on a long series of samples received at various times from various sources necessarily afford a broader survey of the status of any given drug than the occasional analyses of chemists bent on pure research. For the most part, the outlook is encouraging; the drug market was never in a more satisfactory state than at the present time. The majority of drugs comply with the law. Certain drugs are peculiarly subject to adulteration; for example, asafetida and lupulin, and much patient effort must still be expended before such drugs can be brought up to the required standard." C. A. R.

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CHEMICAL JOURNAL

[Contribution from the Kent Chemical Laboratory of the University of Chicago]

ON THE OXIDATION OF *d*-GLUCOSE IN ALKALINE SOLUTION BY AIR AS WELL AS BY HYDROGEN PEROXIDE

By J. W. E. Glattfeld

The oxidation of *d*-glucose in approximately half normal potassium hydroxide solution (9 molecules) by means of hydrogen peroxide has been studied in this laboratory by Spoehr,[1] who found that four oxidation products—namely, small amounts of carbon dioxide (3.51 per cent.), glycollic acid and a new hexonic acid, $C_6H_{12}O_7$, α-hydroxymethyl-*d*-arabonic acid, besides very large amounts of formic acid (65.3 per cent.)—are formed.

Preliminary experiments by Nef had convinced him that Spoehr, in carrying out the very difficult separations by means of alkaloidal salts, must have overlooked the presence of *dl*-glyceric acid and of isomeric trihydroxybutyric acids which are also formed in this oxidation process; and since, furthermore, Nef has recently succeeded in finding a perfectly general method for oxidizing all sugars in very dilute alkaline solutions at low temperatures (40°) with air *without the simultaneous formation of saccharinic acids*, it was now possible to show also by experiment that *d*-glucose, when oxidized in alkaline solution by air, gives exactly the same oxidation products as when hydrogen peroxide is used. The problem therefore assigned to me by Dr. Nef was to determine especially the nature of all the nonvolatile hydroxy acids formed from *d*-glucose in alkaline solution by air as well as by hydrogen peroxide.

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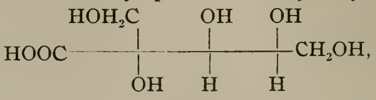
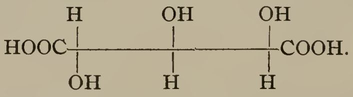
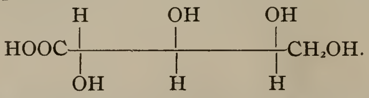
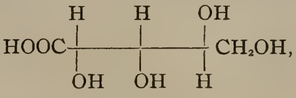
[1] This Journal, **43**, 233–245.

The new hexonic acid considered by Spoehr to be α-hydroxymethyl-*d*-arabonic acid,  $HOOC-\overset{HOH_2C}{\underset{OH}{|}}-\overset{OH}{\underset{H}{|}}-\overset{OH}{\underset{H}{|}}-CH_2OH$, was obtained by him in the form of a thick viscous lactone gum possessing a specific rotation of 72°.5, and he had apparently established its constitution as named by an analysis of its well-crystallized calcium salt, and of its phenylhydrazide, as well as by its oxidation, with loss of carbon dioxide, to *d*-trihydroxyglutaric acid,  $HOOC-\overset{H}{\underset{OH}{|}}-\overset{OH}{\underset{H}{|}}-\overset{OH}{\underset{H}{|}}-COOH$.

I succeeded in obtaining Spoehr's acid in the form of its crystallized γ-lactone melting at 96°–98° and have made an exhaustive study of its crystalline derivatives; it finally became perfectly apparent that the acid was not a new hexonic acid but a pentonic acid identical with Ruff's *d*-arabonic acid,



$$HOOC-\overset{H}{\underset{OH}{|}}-\overset{OH}{\underset{H}{|}}-\overset{OH}{\underset{H}{|}}-CH_2OH.$$

In an exactly similar way Dr. Nef has recently proved that Lucas' so-called new α-hydroxymethyl-*d*-lyxonic lactone,[1] which is obtained in large quantities by oxidizing *d*-galactose in dilute sodium hydroxide solution by air, is identical with the γ-lactone of *d*-lyxonic acid,  $HOOC-\overset{H}{\underset{OH}{|}}-\overset{H}{\underset{OH}{|}}-\overset{OH}{\underset{H}{|}}-CH_2OH$, *i. e.*, an optically active pentonic acid is formed.

[1] Ann. Chem. (Liebig), **376**, 55, footnote.

We have therefore here at last the proof sought for for over nine years past by Nef[1] that all hexose sugars in the form of 1,2-hexosedienols,

$$HOCH = C(OH).\overset{*}{C}H(OH).\overset{*}{C}H(OH).\overset{*}{C}H(OH).\overset{*}{C}H_2OH,$$

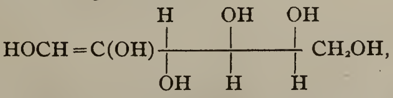
dissociate into hydroxymethylene and various methylenenols of pentose sugars; and since previous experiments by Nef prove very sharply that hexose sugars in the form of 2,3-hexosedienols,

$$HOCH_2.C(OH) = C(OH).\overset{*}{C}H(OH).\overset{*}{C}H(OH).CH_2OH,$$

and 3,4-hexosedienols,

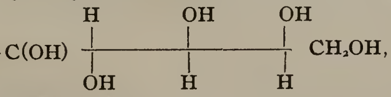
$$HOCH_2.\overset{*}{C}H(OH).C(OH) = C(OH).\overset{*}{C}H(OH).CH_2OH,$$

dissociate into diose and isomeric tetrose sugars as well as into two molecules of glyceraldehydemethylenenol, it is now certain that every hexose sugar in alkaline hydroxide medium, besides giving a mixture of six sugars of the corresponding series,[2] splits spontaneously into a mixture of various sugars containing one, two, three, four and five carbon atoms, $(CH_2O)_x$. The 1,2-*d*-glucosedienol,



$$HOCH{=}C(OH)\underset{OH}{\overset{H}{|}}\!\!-\!\!\underset{H}{\overset{OH}{|}}\!\!-\!\!\underset{H}{\overset{OH}{|}}\,CH_2OH,$$

common to *d*-glucose, *d*-mannose and *d*-fructose, obviously splits into hydroxymethylene, >CHOH, and the methylenenol of *d*-arabinose,



$$>C(OH)\underset{OH}{\overset{H}{|}}\!\!-\!\!\underset{H}{\overset{OH}{|}}\!\!-\!\!\underset{H}{\overset{OH}{|}}\,CH_2OH,$$

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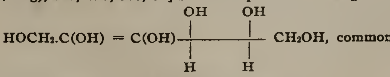
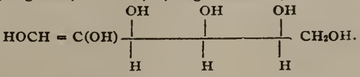
[1] Ann. Chem. (Liebig), **357**, 259; **376**, 52.

[2] *d*-Allose and *d*-latose are *not* present as members of the *d*-glucose series [cf. *Ann.* Chem. (Liebig), **357**, 294; **376**, 87] because *d*-pseudofructose gives only a 2,3-*d*-glucosedienol,



$$HOCH_2.C(OH) = C(OH)\underset{H}{\overset{OH}{|}}\!\!-\!\!\underset{H}{\overset{OH}{|}}\,CH_2OH,$$

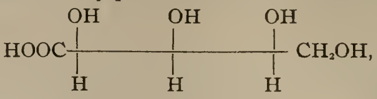
common to it, *d*-fructose and α- and β-*d*-galtose, and not a β-1,2-*d*-glucosedienol,



$$HOCH = C(OH)\underset{H}{\overset{OH}{|}}\!\!-\!\!\underset{H}{\overset{OH}{|}}\!\!-\!\!\underset{H}{\overset{OH}{|}}\,CH_2OH.$$

J. U. Nef.

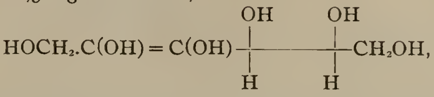
which then mainly takes up oxygen to give *d*-arabonic acid; at the same time it is very probable that some *d*-ribonic acid,



$$\mathrm{HOOC}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{|}}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{|}}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{|}}-\mathrm{CH_2OH},$$

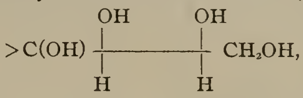
is also formed, but I was unable to establish this experimentally (see below).

The 2,3-*d*-glucosedienol,



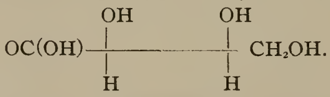
$$\mathrm{HOCH_2.C(OH)=C(OH)}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{|}}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{|}}-\mathrm{CH_2OH},$$

similarly splits into the methylenenols of diose, $\mathrm{HOCH_2.C(OH)} <$, and of *d*-erythrose,



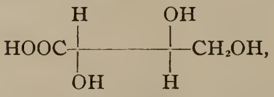
$$> \mathrm{C(OH)}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{|}}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{|}}-\mathrm{CH_2OH},$$

which should therefore take up oxygen to give *d*-erythronic acid,



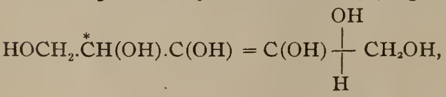
$$\mathrm{OC(OH)}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{|}}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{|}}-\mathrm{CH_2OH}.$$

This was in fact the *chief optically active trihydroxybutyric acid* found by me among the oxidation products of *d*-glucose with air as well as with hydrogen peroxide; at the same time a very small amount of optically active *l*-threonic acid,



$$\mathrm{HOOC}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{|}}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{|}}-\mathrm{CH_2OH},$$

is also unquestionably formed. The 3,4-*d*-glucosedienol,



$$\mathrm{HOCH_2.\overset{*}{C}H(OH).C(OH)=C(OH)}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{|}}-\mathrm{CH_2OH},$$

obviously splits spontaneously as soon as formed into two molecules of glyceraldehydemethylenenol,

$$2\mathrm{HOCH_2.CH(OH).C(OH)} <,$$

which naturally takes up oxygen to give *dl*-glyceric acid, hence this acid was found by me as an oxidation product under the conditions named. In addition, glycollic acid and especially large amounts of formic acid (65.2 per cent. and 14.8 per cent., respectively, with hydrogen peroxide and air) are obtained as oxidation products; these are formed mainly through the direct oxidation of hydroxymethylene, $>CHOH$, and of diosemethylenenol, $HOCH_2C(OH)<$.

Especially noteworthy is the fact that *none* of the six-carbon-atom sugars originally present in the alkaline solution—*d*-glucose, *d*-mannose, *d*-fructose, *d*-pseudofructose and α- and β-*d*-glutose (3-ketohexoses)—actually oxidize to their corresponding hexonic acids. This apparently only happens when Fehling's solution is used.[1] It is still possible that small quantities of *d*-mannonic and *d*-gluconic acids are formed when *d*-glucose (or any other of the six components of the *d*-glucose series) is oxidized in alkaline solution by air or hydrogen peroxide, but I was unable to establish their presence by experiment.

EXPERIMENTAL PART

I. The Action of Hydrogen Peroxide on d-*Glucose in Alkaline Solution*

In order to obtain as much nonvolatile hydroxy acid gum as possible, 75 grams of *d*-glucose were dissolved in two liters of cold three per cent. hydrogen peroxide and six equivalents of concentrated sodium hydroxide solution (102 grams of ninety-eight per cent. sodium hydroxide in 240 cc. water) were then slowly added in approximately equal portions, one equivalent immediately and the others at the end of 5, 9, 23, 27 and 32 hours, respectively. One hundred cc. more hydrogen peroxide were added at the end of 29 hours and when all the alkali had been introduced—at the end of 32 hours—465 cc. more hydrogen peroxide were added, so that the total volume of the solution rose to about three liters. The mixture was then allowed to stand 39 hours longer at ordinary temperature, when the test for sugar had become very faint, whereas the solution still gave—as throughout every stage in the oxidation process—a strong test for hydrogen peroxide.

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[1] Cf. Nef: Ann. Chem. (Liebig), **357**, 259–286.

Four such portions of seventy-five grams of *d*-glucose were worked up simultaneously, as well as another portion of 50 grams of *d*-glucose in 1500 cc. three per cent. hydrogen peroxide, to which, however, the six equivalents of sodium hydroxide in a small amount of cold water had been added in portions in the course of five days instead of 32 hours as in the other four cases.

At the end of seventy-one hours each of the four solutions was concentrated by distillation at 50° under 40 mm. pressure to about 800 cc. A test for sugar at this point showed none to be present. The solutions were then extracted twice with ether in order to remove small amounts of aniline formed by the hydrolysis of acetanilide which was present in very small amounts in the commercial hydrogen peroxide used. They were then acidified with concentrated hydrochloric acid. Twice the amount necessary to neutralize the alkali used was added. On distilling to a small volume at 60° under 30 mm. pressure, large amounts of sodium chloride had separated out. About two liters of 95 per cent. alcohol was now added to the mixture. The sodium chloride was filtered off and washed thoroughly with 95 per cent. alcohol. The filtrates were then distilled off completely at 60° under 30 mm. pressure and the residue was thoroughly extracted with absolute alcohol. At this stage the corresponding absolute alcohol extract obtained from the above-mentioned oxidation of 50 grams of *d*-glucose was combined with those obtained from 300 grams *d*-glucose as just stated, and the alcohol was then removed by distillation at 60° under 20 mm. pressure, giving thus a total of 83 grams crude brown nonvolatile gums, from 350 grams *d*-glucose, which still contained a very small amount of sodium chloride.

These gums were now resolved by two successive digestions with one liter of ethyl acetate into two soluble fractions:[1] 39 grams with $[\alpha]_D^{20}$ 33°.97 and 6.5 grams with $[\alpha]_D^{20}$ 47°.08, after freeing from ethyl acetate, etc., by sweeping over with water at 80° under 20 mm. pressure. These fractions were again united and extracted four times with one liter of ether and thus a total of 17.45 grams soluble gums, *A*, with $[\alpha]_D^{20}$ 23°.78, was obtained, leaving 25.5 grams gums, *B*, undissolved. The portion of the original 83 grams gums left undissolved by ethyl acetate was found to weigh 31 grams, gum *C*, with $[\alpha]_D^{20}$ 44°.35. Since *d*-arabonic acid gives a very difficultly soluble phenylhydrazide, and it was obviously not possible to separate the nonvolatile hydroxy acids to any appreciable degree by fractional solution in solvents, I decided to treat the gums *A*, *B* and *C* with phenylhydrazine. This was invariably done by mixing the gums with a volume each of phenylhydrazine and absolute alcohol equal to the weight of the gum taken, warming gently and stirring until a homogeneous mixture resulted. The crystalline hydrazide separated out completely in the course of 24 hours' standing at ordinary temperature, and was then filtered off and washed until snow-white with absolute alcohol. The gummy hydrazides left in the alcoholic filtrates were freed from alcohol by distillation under 20 mm. pressure in a bath kept at 40°–50°, and then freed from the excess of phenylhydrazine by threefold extraction in aqueous solution with ether. On removal of the water by distillation under reduced pressure, and dissolving the residue in eight parts of absolute alcohol, usually a fair amount more of crystalline hydrazide separated out. In this way I obtained from the above-mentioned three gums a total of 72.15 grams of acid hydrazides melting from 195° to 209°, as follows: Gum *A*, 17.45 grams, gave 8.8 grams crystals melting from 205° to 209°; Gum *B*, 25.5 grams, gave 25.95 grams crystals melting from 195°–204°; Gum *C*, 31 grams, gave 30.1 grams crystals melting from 195°–200°. The combined alcoholic filtrates, treated as stated above, gave 54 grams of gummy hydrazides which, dissolved in 400 cc. absolute alcohol, gave 7.3 grams more of crystals melting at 195°, and the gummy hydrazides left in the filtrate, 45 grams, hydrolyzed 7 hours on a boiling water bath with 45 grams barium hydroxide, 45 cc. water, etc. (see below), gave back 19 grams of nonvolatile hydroxy acids (see below) which were found to be optically inactive.

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[1] All the optical determinations in the entire course of this work were made in approximately 4 per cent. aqueous solution.

The Conversion of the Crude d-*Arabonic Phenylhydrazide into* γ-d-*Arabonic Lactone*

The 72.15 grams of crude *d*-arabonic phenylhydrazide obtained as just described were now hydrolyzed by heating 7 hours on a boiling water bath with 72 grams of crystallized barium hydroxide and 72 cc. water, taking care to shake from time to time. Much water was then added and the solution was filtered; the solids on the filter paper were then washed free of phenylhydrazine with ether and the filtrate also extracted five times with ether in order to remove the phenylhydrazine. The extracted solids and filtrate were then united and the barium precipitated in the usual manner, taking care to leave a trace of barium finally in the clear filtrate, which was then digested with charcoal. The crude *d*-arabonic lactone gum obtained after the customary removal of the water and extraction of the residue with absolute alcohol weighed 34 grams, $[\alpha]_D^{20}$ 60°.73, whereas the amount demanded by theory is 42 grams.

Nef has repeatedly emphasized[1] the fact that it is impossible to convert any polyatomic tetronic, pentonic or hexonic acid quantitatively into its γ-lactone. He has recently succeeded in isolating the pure β and γ monomolecular lactones of *d*-mannonic and *d*-gluconic acid.[2] *d*-Arabonic acid must therefore also give two lactones and this explains, in part at least, why I did not succeed in transforming the 34 grams of crude lactone gums quantitatively into the pure γ-lactone. Since, according to Nef's observations, the γ-lactone is invariably formed in larger ratio at higher temperatures, the method of procedure to obtain the γ-lactone is as follows: The crude lactone is first extracted with hot ethyl acetate and as much crystallized lactone is then obtained from the clear filtrate as possible by concentration, seeding, etc. As soon as the ethyl acetate solutions give no more crystals, the solvent is removed by distillation under reduced pressure and the residual β,γ-lactone mixture then heated in concentrated aqueous solution for 5 hours on a boiling water bath. The water is then removed by distillation at high pressure and temperature, 80°–100°, and the gum then finally kept at 100° for some time under a pressure of 20 mm. This residue will then give more γ-lactone crystals with ethyl acetate, etc.

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[1] Ann. Chem. (Liebig), **357**, 236.

[2] Soon to be published as a thesis by O. F. Hedenburg in This Journal.

I succeeded in this way in obtaining a total of 23.18 grams crude γ-*d*-arabonic lactone crystals, which melted at about 96°, from the above-mentioned 34 grams of crude lactone mixture; and in addition 9 grams of gummy lactones, $[\alpha]_{\mathrm{D}}^{20}$ 52.08°, were obtained from the ethyl acetate filtrates which were treated with brucine as described further on.

Pure γ-d-*Arabonic Lactone.*—On decolorizing with animal charcoal the aqueous solution of 11 grams crude γ-*d*-arabonic lactone crystals which consisted in part of the 23.18 grams mentioned above and in part of the 4.49 grams of similar γ-*d*-arabonic lactone crystals obtained in the air experiment, distilling the solution at 100° under 20 mm. pressure, taking up the residual gum in ethyl acetate and concentrating this solution under reduced pressure, I obtained in all 8.23 grams of beautiful, transparent, hard, measurable crystals melting at 96° to 98°. Ruff[1] gives the melting point of *d*-arabonic lactone as 97°–98° and its specific rotation as 73°.73 (in 10 per cent. concentration). Since it was not possible to determine by analysis whether a pentonic or a hexonic lactone was present, this was determined in favor of *d*-arabonic lactone by four independent titrations by two observers, Dr. Upson and myself, with 0.1 N alkali. Furthermore, I obtained a specific rotation of 68°.94 and 69°.68, respectively, for the crystals in four per cent. aqueous solution as follows:

(*a*) 0.6009 gram substance and 14.6303 grams water gave α in a 1 dcm. tube = 2°.75; and

(*b*) 0.4179 gram substance and 10.6952 grams water gave α in a 1 dcm. tube = 2°.65.

The analysis of 0.2149 gram substance gave 0.1054 gram H_2O and 0.3183 gram CO_2.

	Calculated for $C_5H_8O_5$	Found
C	40.54	40.40
H	5.40	5.49

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[1] Ber. d. chem. Ges., **32**, 557.

Titration of the Lactone.—(1) 0.5298 gram lactone required 34.2 cc. 0.1 N sodium hydroxide for neutralization; the calculated value for $C_5H_8O_5$ is 35.8 cc. and for $C_6H_{10}O_6$, 29.78 cc.

(2) 0.4179 gram lactone required 26.3 cc. 0.1 N sodium hydroxide; calculated for C_5 lactone 28.24 cc. and for C_6 lactone 23.48 cc.

(3) 0.6009 gram lactone required 40.3 cc. 0.1 N sodium hydroxide; calculated for C_5 is 40.6 cc. and for C_6 is 33.76 cc.

(4) 0.603 gram lactone required 41.0 cc. 0.1 N sodium hydroxide (Upson); calculated for C_5 lactone is 40.75 cc. and for C_6 33.88 cc.

d-Arabonic lactone was therefore unquestionably present and this was further established by the analysis of the acid hydrazide and the calcium salt.

d-*Arabonic Phenylhydrazide.*—This compound was formed quantitatively by mixing 1 gram of pure lactone crystals with one volume each of phenylhydrazide and absolute alcohol. The crystals, which had separated out completely after 24 hours, were washed until snow-white with absolute alcohol and melted, after drying on a clay plate and *in vacuo* over sulphuric acid, between 213° and 214°. Ruff[1] gives the melting point of *d*-arabonic phenylhydrazide as 214°. The melting point of the antipode, *l*-arabonic phenylhydrazide, is likewise 214°, and its specific rotation in two per cent. aqueous solution has been determined by Nef as 14°.94, while Spoehr[2] gives —13°.9 as the specific rotation of the *d*-arabonic hydrazide in two per cent. aqueous solution. The analysis of my product shows very clearly that a pentonic and not a hexonic phenylhydrazide is at hand.

0.2852 gram substance gave 0.5384 gram CO_2 and 0.1612 gram H_2O.

0.2292 gram substance gave 22.4 cc. N_2 at 22°.3 C. under 729.9 mm. pressure.

	Calculated for		Found
	$C_{11}H_{16}O_5N_2$	$C_{12}H_{18}O_6N_2$	
C	51.54	50.35	51.49
H	6.30	6.29	6.32
N	10.94	9.79	10.86

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[1] *Loc. cit.*

[2] THIS JOURNAL, **43**, 240.

Calcium d-*Arabonate*, $(C_5H_9O_6)_2Ca.5H_2O$.—The crystallized calcium salt here studied was made from a gummy lactone obtained from crude *d*-arabonic brucine crystals (melting point, vacuum dried, 170°–176°) by hydrolysis. After the calcium determinations given below had been made the rest of this calcium salt—11.78 grams—was converted by the usual method into 6.56 grams gummy lactone; 5.29 grams of this gum gave with ethyl acetate, etc., 3.87 grams crystallized γ-*d*-arabonic lactone melting about 95° and with $[\alpha]_D^{20}$ 68°.65.

Three determinations of the calcium content of this salt were made. According to Ruff[1] this salt crystallizes with 5 molecules of water—the same is also true of its antipode—which cannot be removed *in vacuo* over sulphuric acid.

I. 0.2380 gram vacuum-dried salt gave 0.0292 gram CaO.
II. 0.2312 gram salt gave 0.0284 gram CaO.
III. 0.2730 gram salt gave 0.0338 gram CaO.

see errata, p. 514.

	Calculated for	Found		
	~~$(C_5H_{10}O_6)_2Ca.5H_2O$~~	I	II	III
Ca	8.71	8.77	8.78	8.85

The specific rotation of this salt, calculated for the anhydrous salt, was found to be, in agreement with Spoehr,[2] —3°.19 : 0.5656 gram salt dissolved in 13.4431 grams water gave α in a 1 dcm. tube = —0°.105, whence $[\alpha]_D^{20}$ for the hydrated salt is —2°.57 and for the anhydrous salt —3°.19.

Cinchonine d-*Arabonate*.—On heating an aqueous solution of 1 gram crude γ-lactone crystals for 4 hours on a boiling water bath with an excess of cinchonine, filtering off the undissolved alkaloid and distilling the clear solution at 70° under 20 mm. pressure, 2.50 grams of crude salt were obtained which required 30 cc. of hot absolute alcohol for solution. The clear filtrate deposited 1.08 grams of salt in the form of hard, radiating needles, melting between 178° and 180°, and possessing $[\alpha]_D^{20}$ 120°.3, *i. e.*, 0.405 gram salt and 9.9887 grams water gave α in a 1 dcm. tube = 4°.74.

Since Nef[3] has shown that cinchonine *l*-arabonate is a gummy salt very soluble in cold absolute alcohol—an observation which I have confirmed—it is evident that *dl*-arabonic lactone can easily be resolved into its optical components by means of cinchonine. It follows also from this that the cinchonine *d*-gluconate obtained by Nef in his oxidation experiments with *d*-glucose, *d*-mannose, and *d*-fructose and Fehling's solution[1] must have contained cinchonine *d*-arabonate which—unlike its antipode—is also very difficultly soluble in absolute alcohol. Dr. Nef informs me that he feels certain that this was the case because the melting point of the cinchonine *d*-gluconate obtained by him in these experiments was not sharp (189°) but ranged from 170° to 187°. Furthermore, he noticed especially that on setting free the *d*-gluconic gum from this salt mixture he had great difficulty in obtaining sufficient crystallized calcium *d*-gluconate (even on seeding) for his optical determinations.

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[1] *Loc. cit.*

[2] THIS JOURNAL, **43**, 241.

[3] Ann. Chem. (Liebig), **357**, 227.

Strychnine d-*Arabonate.*—The crude lactone crystals, 1.03 grams, were digested in aqueous solution with an excess of strychnine until no more alkaloid dissolved and after removal of the water 3.28 grams of crude crystalline salt were obtained. This was practically insoluble in hot absolute alcohol but dissolved in a hot mixture of 9 cc. water and 60 cc. absolute alcohol. Fine feathery needles then separated out from the filtrate. They lost very little water on drying over sulphuric acid *in vacuo*, and weighed 2.3 grams after so drying. These crystals decomposed between 167° and 170° and gave $[\alpha]_D^{20} = -26°.08$, *i. e.*, 1.055 grams salt and 24.2331 grams water gave α in a 2 dcm. tube $= -2°.20$.

Quinine d-*Arabonate.*—This substance was made from 1.0 gram of the crude lactone crystals with the theoretical amount of quinine. The crude salt, 2.9 grams, dissolved in a hot solution of 3 cc. water and 30 cc. absolute alcohol, deposited a hard crust of indistinguishable crystals, 1.35 grams, melting from 172° to 173° and giving $[\alpha]_D^{20}$ $-106°.2$; *i. e.*, 0.3589 gram substance and 8.7741 grams water gave α in a 1 dcm. tube $= -4°.22$.

Brucine d-*Arabonate.*—This especially characteristic salt of

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[1] Ann. Chem. (Liebig), **357**, 267–270, 276, 281.

d-arabonic acid crystallizes from one-third its weight of water and three parts of alcohol in transparent plates melting from 167° to 170°; these lose 5.6 per cent. crystal water and become opaque on drying over sulphuric acid *in vacuo*, but the melting point remains unchanged. The specific rotation was found to be —26°.33, *i. e.*, 1.0555 grams salt and 25.3245 grams water gave α in a 2 dcm. tube = —2°.13. It is obvious from Spoehr's description of this salt[1] that it was at times contaminated with the high-melting (210°–220°) brucine salts of *dl*-glyceric, *d*-erythronic and *l*-threonic acids.

On the Constants of l-*Arabonic Lactone and its Derivatives.*—For the sake of comparison and to show more decisively, if possible, that the *d*-arabonic lactone obtained by me is the real antipode of the long-known *l*-arabonic lactone, I summarize here the various constants obtained by me and by other observers for *l*-arabonic lactone and its most characteristic derivatives. According to Nef's latest observations, 36.93 grams crude γ-*l*-arabonic lactone crystals give, when dissolved in 500 cc. hot acetone and filtered from a small amount of insoluble tar, by concentration to a small volume, 31.6 grams large, heavy, measurable, transparent crystals melting from 98° to 101° and possessing $[\alpha]_D^{20}$ —72°.2, *i. e.*, 0.4964 gram substance and 11.9138 grams water gave α in a 1 dcm. tube —2°.92. The specific rotation of the beautifully crystallized calcium salt, $(C_5H_9O_6)_2Ca.5H_2O$, is known to be 3°.1. I have made the brucine and strychnine salts of *l*-arabonic acid in the usual manner from 0.5 gram of Nef's purest γ-lactone (see above). The well-dried brucine salt melted at 160° and the strychnine salt at 117° (air dried) and 164° after drying *in vacuo*. Nef[2] gives the melting point of the vacuum-dried *l*-arabonic brucine as 155° and its specific rotation he has found to be —21°.74 (p = 4.0); the melting point of the air-dried strychnine salt was between 125° and 130°, and its specific rotation he has determined as —19°.1 (p = 4). The specific rotation of the phenylhydrazide has been determined by Nef as 14°.94 in two per cent. concentration (see above).

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[1] This Journal, **43**, 239.

[2] Nef: Ann. Chem. (Liebig), **357**, 227.

On the Unidentified Lactone Gums Obtained from the 72.15 Grams Crude d-*Arabonic Phenylhydrazide.*—As mentioned above, 9 grams of gummy lactones, $[\alpha]_D^{20}$ 52°.08, were obtained, besides 23.18 grams crude crystallized *d*-arabonic lactone, from 34 grams crude lactone gums. These were digested with 22 grams brucine, the heating being continued—as was customary—for one hour after the alkaloid had been dissolved. The cold aqueous solution was extracted three times with benzene and 35 grams of a crystalline residue obtained after removal of the water by distillation at reduced pressure. This residue, dissolved in a mixture of 10 cc. water and 160 cc. of absolute alcohol, deposited on standing 15.70 grams of crystals melting at 165° and possessing the characteristic appearance of *d*-arabonic brucine. The mother liquor then gave 15.7 grams crystalline brucine salts on distillation which, digested with 800 cc. absolute alcohol, left 0.95 gram insoluble salt melting at 195°. This may have been brucine *d*-mannonate, but I was unable to prove it by experiment. Furthermore, I was unable to establish the nature of the 14.75 grams salts dissolved by the 800 cc. absolute alcohol; I tried, for instance, to prove the presence of *d*-gluconic acid therein by conversion into the cinchonine salts, but without success. Since Nef has obtained small quantities of *l*-ribonic acid, as well as much *l*-arabonic acid, by the action of Fehling's solution on *l*-arabinose,[1] it is extremely probable that *d*-ribonic acid, which gives no well-defined alkaloid derivatives, was mainly present.

d-*Erythronic Lactone,* l-*Threonic Phenylhydrazide and* dl-*Glyceric Acid from the 19 Grams Optically Inactive Gums.*—The 19 grams inactive gums obtained by the hydrolysis of the 45 grams alcohol-soluble gummy hydrazides were digested in aqueous solution with 65 grams of brucine and then extracted as usual with benzene. Eighty-two grams of crystalline salts were left in the distilling flask after the removal of the water. These were dissolved in a hot mixture of 41 cc. water and 205 cc. of absolute alcohol and 15 grams of practically pure brucine *d*-erythronate melting at 209° separated out in plates on standing overnight. On crystallizing these from one-half a part of water and five parts of alcohol, 12.98 grams of thick crystal plates melting from 212° to 214° and possessing $[\alpha]^{20}_{\mathrm{D}}$ —25°.62 separated out. Ruff gives $[\alpha]^{20}_{\mathrm{D}}$ —23°.5 as the specific rotation of absolutely pure brucine *d*-erythronate.

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[1] Ann. Chem. (Liebig), **357**, 231.

γ-d-*Erythronic Lactone.*—On treating the 12.98 grams salts in aqueous solution with one and one-half times the calculated amount of hot aqueous barium hydroxide, filtering off the brucine and removing traces left in the alkaline solution by fivefold extraction with benzene, etc., 2.5 grams of lactone gum was obtained which solidified almost entirely on cooling. Since the sticky residue gave $[\alpha]^{20}_{\mathrm{D}}$ —71°.0, practically pure γ-d-erythronic lactone must have been present. The substance was therefore dissolved in hot ethyl acetate and on concentration to a small volume, 1.82 grams of the pure lactone was obtained in colorless prisms melting from 102° to 103° and possessing $[\alpha]^{20}_{\mathrm{D}}$ —73°.11, *i. e.*, 0.299 gram substance and 6.99 grams water gave α in a 1 dcm. tube = —3°.03. Ruff[1] gives —73°.3 as the specific rotation in 8 per cent. concentration and 103° as the melting point of this lactone. The amount of 0.1 N sodium hydroxide necessary for the neutralization of 0.4028 gram of this lactone was 33.3 cc. instead of 34.14, which is the amount demanded theoretically by $C_4H_6O_4$.

0.1792 gram of the lactone gave 0.0791 gram H_2O and 0.2661 gram CO_2.

	Calculated for $C_4H_6O_4$	Found
C	40.68	40.50
H	5.12	49.4

d-*Erythronic Phenylhydrazide.*—The 0.299 gram lactone used in the above-mentioned determination of specific rotation was treated in the customary manner with 0.3 cc. phenylhydrazide and alcohol. Owing to its great solubility only 0.3 gram phenylhydrazide melting from 119° to 120° was obtained. On crystallizing from a small amount of hot ethyl acetate 0.15 gram crystals melting at 125° and giving $[\alpha]^{20}_{\mathrm{D}}$ 17°.10 was obtained, *i. e.*, 0.145 gram substance and 3.435 grams water gave α in a 0.5 dcm. tube = 0°.35. Ruff[1] gives the melting point as 128° and the specific rotation as 17°.5.

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[1] Ber. d. chem. Ges., **32**, 3679–80.

Strychnine d-*Erythronate.*—Recent experiments by Nef and myself have proved that *d*-erythronic and *l*-threonic acids give especially beautiful, well-crystallized and very difficultly alcohol-soluble salts; these, however, can not be used as a means of separating these acids from glycollic and *dl*-glyceric acids because of the formation of mixed crystals (see below).

Pure strychnine *d*-erythronate was made from 0.5 gram of pure *d*-erythronic lactone by digestion in aqueous solution with an excess of powdered strychnine. As the crude salt, 1.9 gram, was found to dissolve with the greatest difficulty in hot absolute alcohol, it was crystallized from 2 cc. water and 10 cc. absolute alcohol; there separated out on standing overnight 0.9 gram of radiating needles melting from 198° to 199° and possessing $[\alpha]_D^{20}$ —16°.84, *i. e.*, 0.2912 gram salt and 6.8933 grams water gave α in a 1 dcm. tube = —0°.69.

Quinine d-*Erythronate.*—The pure lactone, 0.5 gram, and the theoretical amount of quinine gave 1.95 grams crude salt. This, dissolved in 20 cc. hot absolute alcohol, gave a crop of long radiating hair-like needles weighing 0.8 gram and melting at 166° with $[\alpha]_D^{20}$ —106°.9; *i. e.*, 0.3384 gram salt and 7.9726 grams water gave α in a 1 dcm. tube = —44°.4.

l-*Threonic Phenylhydrazide.*—The alcoholic filtrate from the 15 grams crude brucine *d*-erythronate mentioned above still contained 61 grams brucine salts which, digested with 400 cc. absolute alcohol and allowed to stand overnight, yielded 29.6 grams insoluble salts melting at 197°. After several crystallizations of this fraction from one part water and ten parts absolute alcohol, 4.93 grams salts melting at 210° and possessing $[\alpha]_D^{20}$ —27.23° were obtained. These gave 0.9 gram lactone gum, $[\alpha]_D^{20}$ —33°.89, which yielded on the customary treatment with phenylhydrazine 0.37 gram (in two crops) crude *l*-threonic phenylhydrazide melting at 155° and giving $[\alpha]_D^{20}$ —25°.18. Since *l*-threonic phenylhydrazide, according to Anderson,[2] melts at 158°, crystallizes in transparent plates and possesses $[\alpha]^{20}_{\mathrm{D}}$ —31°.17 (Nef found $[\alpha]^{20}_{\mathrm{D}}$ —28°.78 in two independent determinations), it is obvious that *l*-threonic acid is also an oxidation product of *d*-glucose by alkaline hydrogen peroxide, but it is formed in decidedly smaller amounts than its isomer, *d*-erythronic acid. In this connection it is interesting to note that *d*-galactose, when oxidized in alkaline solution by air, hydrogen peroxide, or Fehling's solution, gives, according to Nef's latest observations, relatively far larger amounts of *l*-threonic acid than of *d*-erythronic acid. This can be understood *only* on the assumption that the methylenenol of *d*-erythrose and *l*-threose which must be formed respectively by the dissociation of 2,3-*d*-glucosedienol,

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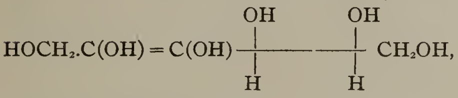
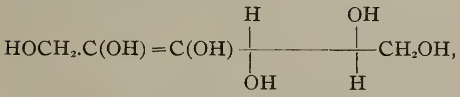
[1] *Loc. cit.*

[2] THIS JOURNAL, **42**, 424.



$$\mathrm{HOCH_2.C(OH)=C(OH)}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{|}}-\!-\!-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{|}}-\mathrm{CH_2OH},$$

and of 2,3-*d*-galactosedienol,



$$\mathrm{HOCH_2.C(OH)=C(OH)}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{|}}-\!-\!-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{|}}-\mathrm{CH_2OH},$$

must in each case mainly take up oxygen directly, *i. e.*, before being transformed into ordinary *d*-erythrose and *l*-threose.

dl-*Glyceric Acid.*—On setting free the acids from the brucine salts still left in the alcoholic filtrates, 45 grams by actual determination, by means of barium hydroxide, etc., 9.0 grams of gum, $[\alpha]^{20}_{\mathrm{D}}$ 16°.67, were recovered. This shows very clearly that a large amount of *d*-arabonic acid must still have been present in the above-mentioned 19 grams of inactive gums obtained from the hydrolysis of the gummy alcohol-soluble phenylhydrazide. The 9 grams of gum were accordingly extracted with half a liter of hot ether and a resolution into 1.86 grams soluble gum, $[\alpha]^{20}_{\mathrm{D}}$ 3°.76, and 6 grams insoluble gum, $[\alpha]^{20}_{\mathrm{D}}$ 21°.66, was thereby effected. The usual treatment of the 6 grams gum with phenylhydrazine removed 1.25 grams *d*-arabonic phenylhydrazide, melting at 195° to 200°. Hydrolysis of the alcohol-soluble hydrazides—including those obtained in treating the above-mentioned 0.9 gram crude *l*-threonic gum, $[\alpha]_D^{20}$ —33°.89, with phenylhydrazine—gave back 3.96 grams acid gums, $[\alpha]_D^{20}$ 2°.5, which were therefore combined with the 1.86 grams of above-mentioned ether-soluble gums. These gave with brucine, etc., a total of 6.33 grams of high-melting (209°–214°) brucine salts which on hydrolysis gave 1.35 grams gum, $[\alpha]_D^{20}$ —10°.6. The C_4 gums—mainly *d*-erythronic—present in this gum were now removed by conversion into strychnine salts; 0.55 gram salts melting at 190° separated out on seeding and long standing. The alcoholic filtrate then gave back by barium hydroxide, etc., 1.25 grams gum, $[\alpha]_D^{20}$ 4°.4. The acid gums obtained from the 6.33 grams high-melting brucine salts by means of barium hydroxide, etc., weighed 2.77 grams and gave $[\alpha]_D^{20}$ 13°.7. Various attempts were made to resolve this gummy mixture by means of solvents (ethyl acetate) and alkaloids (strychnine) but without success, so that finally the recovered gums, about 1.75 grams, were united with the 1.25 grams gum, $[\alpha]_D^{20}$ 4°.4, which had given high-melting brucine salts (see above). The presence of a fair amount of *dl*-glyceric acid in this mixture was now unquestionably established by conversion of the combined gum, 3 grams, by digestion with quinine, subsequent extraction of the aqueous solution with ether to remove excess of alkaloid, and crystallization of the salts obtained, 12.15 grams, from water. A total of 3.7 grams of the very difficultly water-soluble quinine[1] *l*-glycerate, melting at 176°, separated out (in two crops) from the aqueous solution on standing. Over half of the total quinine salts obtained must therefore have consisted of quinine *dl*-glycerate.

II. On the Oxidation of d-*Glucose in Alkaline Solution by Air*

Fifty grams of *d*-glucose in a small amount of water were added to a cold solution of 68 grams of 98 per cent. sodium hydroxide (six equivalents) in 5 liters of water. A rapid stream of air was at once started through the solution by means of four tubes, each drawn out into six capillaries arranged in a starfish form. This enabled the air bubbles—which were first drawn through two sets of two concentrated aqueous potassium hydroxide solutions connected by two Y-tubes with the four entrance tubes—to become scattered through the whole solution. Two powerful water pumps were necessary and the air stream was continued night and day for 46 hours. The temperature of the large water bath surrounding the round-bottom six-liter flask containing the sugar solution varied between 30° and 40°. No trace of sugar was found in the perfectly colorless alkaline solution at the end of the experiment. The exact amount of hydrogen chloride necessary to neutralize the sodium hydroxide used was now added and the water and formic acid were then removed by distillation under 20 mm. pressure, taking care to sweep over all the formic acid by redissolving in water, etc.

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[1] This Journal, **42**, 421.

Determination of the Formic Acid.—The total amount of aqueous distillate, giving a barely perceptible opalescence with silver nitrate, was 5355 cc. One hundred cc. of this required 46.1 cc. 0.0999 N potassium hydroxide for neutralization (phenolphthalein), which is equivalent to 0.2118 gram formic acid; hence the total amount of formic acid formed from 50 grams *d*-glucose was 11.35 grams (14.8 per cent.).

The Nonvolatile Gummy Acids.—The residue in the distilling flask was now treated in aqueous solution with 160 cc. concentrated (36 per cent.) hydrochloric acid in order to insure the complete liberation of all organic acids. The residual gums, smelling therefore strongly of hydrochloric acid, were freed from sodium chloride in the usual manner; 36 grams of lactone gums, giving $[\alpha]_D^{20}$ 22°.98, and still containing small amounts of sodium chloride, were finally obtained, which shows that the yield of nonvolatile hydroxy acids is enormous when compared with the corresponding experiment with hydrogen peroxide. The gum was now resolved by digestion with half a liter of ethyl acetate into a soluble fraction, 26 g.; and an insoluble portion which, when freed from a small amount of sodium chloride by means of absolute alcohol, weighed 11 grams—gum *C*—and gave $[\alpha]_D^{20}$ 34°.27.

The soluble fraction was further resolved by thorough extraction with ether—four times with a half liter each time—into 12.8 grams ether-soluble gums, *A*, with $[\alpha]_D^{20}$ 10°.70, and into 12.2 grams ether-insoluble gums, *B*, with $[\alpha]_D^{20}$ 36°.48. Gums *B* and *C* were now treated in the usual manner with phenylhydrazine and absolute alcohol; the former gave 8.25 grams phenylhydrazides melting at 210° and the latter gave 5.7 grams of similar crystals melting at 193°. These two crops were therefore united and worked up for *d*-arabonic lactone after adding 1.9 grams hydrazides, melting at 195°, subsequently obtained from the combined alcoholic filtrates by distilling off the alcohol *in vacuo*, dissolving in water, extracting with ether, etc. The gummy alcohol-soluble phenylhydrazides, 18 grams, then gave back on the usual hydrolysis with barium hydroxide, etc., 10 grams lactone gums, $[\alpha]_D^{20}$ 5°.75.

γ-d-*Arabonic Lactone.*—Hydrolysis of the combined high melting phenylhydrazides, 15.85 grams, by barium hydroxide now gave 8.0 grams of crude *d*-arabonic lactone gums. I succeeded in obtaining from these by extraction with ethyl acetate, digestion with water, etc., as described in Part I, 4.49 grams of crystallized γ-*d*-arabonic lactone giving $[\alpha]_D^{20}$ 67°.70, *i. e.*, 0.6093 gram lactone and 14.5007 gram water gave α in a 1 dcm. tube = 2°.76.

The total amount of the noncrystallizable lactone gums found in the filtrates was 3.0 grams; from these I obtained by conversion into brucine salts and subsequent crystallization only 3.3 grams of transparent crystalline plates melting from 167° to 170° and obviously consisting of brucine *d*-arabonate. It is, however, possible in this case also that a small amount of *d*-mannonic as well as of *d*-gluconic acid, and especially also some *d*-ribonic acid, was present, but I was unable to prove this by experiment.

d-*Erythronic Lactone and* dl-*Glyceric Acid.*—The *A* gums, 12.8 grams, $[\alpha]_D^{20}$ 10°.7, and the 10 grams gums $[\alpha]_D^{20}$ 5°.75, obtained from the alcohol-soluble gummy hydrazides from the *B* and *C* gums, obviously still contained a fair amount of *d*-arabonic lactone. I found first that it was possible to effect a considerable resolution of this gummy mixture by dissolving the gums partially in ten parts of hot acetic ester and then extracting the soluble portion with one hundred parts of hot ether. The ten-gram portion, for instance, was thus resolved into three fractions: 3.0 grams, $[\alpha]_D^{20}$ —1°.6; 1.5 grams, $[\alpha]_D^{20}$ 6°.0; and 5.0 grams, $[\alpha]_D^{20}$ 11°.2, arranged in the order of solubility. Similarly, 9.5 grams of gum, $[\alpha]_D^{20}$ 10°.5, was resolved by digestion with half a liter of ether into 1.5 grams optically inactive soluble gums, and into 6.5 grams insoluble gums, $[\alpha]_D^{20}$ 18°.49; the latter then gave with phenylhydrazine 1.35 grams more *d*-arabonic phenylhydrazide, melting at 195° to 210°. Furthermore, I also tried conversion of the various gums into brucine salts in the hope of being able to accomplish a sharp separation of the high-melting (210° to 220°) brucine salts of *d*-erythronic, *dl*-glyceric and *l*-threonic acids from brucine *d*-arabonate which melts at 167° to 170°. I was unsuccessful in this, as I obtained large amounts of mixed crystals of these various salts, melting in the neighborhood of 180° to 200°. It was therefore with very great difficulty, and after many recrystallizations, that I finally obtained from the above-mentioned 22.8 grams of unidentified gums a total of 9.87 grams crude brucine *d*-arabonate melting from 150° to 170°, and 21.29 grams brucine salts melting from 208° to 214°. The latter then gave on treatment with barium hydroxide 4.15 grams lactone gum, $[\alpha]_D^{20}$ —10°.0, which on treatment with excess of strychnine took up 10.35 grams of this alkaloid. On distilling there was obtained a crystalline residue weighing 16 grams which gave two crops of salts on crystallization from spirit; 2.86 grams melting at 180° to 198°, with $[\alpha]_D^{20}$ —19°.43, and 2.38 grams melting at 130° to 150°, with $[\alpha]_D^{20}$ —18°.85. The former gave 0.8 gram lactone, $[\alpha]_D^{20}$ —44°.37, and the latter gave 0.57 gram gum, $[\alpha]_D^{20}$ 1°.7, which shows therefore the presence of small amounts of *d*-arabonic lactone.

The 0.8 gram gum, $[\alpha]_D^{20}$ —44°.37, solidified on cooling and gave, on crystallizing from a small amount of ethyl acetate, 0.3 gram of crude *d*-erythronic lactone, melting at 95°, and possessing $[\alpha]_D^{20}$ —66°.79, *i. e.*, 0.1085 gram lactone and 3.0495 grams water gave α in a 0.5 dcm. tube = —1°.16.

The 0.57 gram gum, $[\alpha]_D^{20}$ 1°.7, obtained from the second crop of strychnine salts, contained *dl*-glyceric acid mainly, for it gave on conversion into its quinine salt (1.74 grams obtained) a crop of 0.5 gram of quinine *l*-glycerate melting at 175° on crystallizing the salt from water.

Finally two other slightly active gums—2.95 grams, $[\alpha]_D^{20}$ 5°.7, and 2.33 grams, $[\alpha]_D^{20}$ 0°.86, the latter having been obtained from the alcohol-soluble strychnine salts from the above 4.15 grams lactone gum, $[\alpha]_D^{20}$ —10°.0—were converted into quinine salts. These gums took up 16 grams quinine and gave a crystalline residue of 25 grams. This residue gave on crystallization from water a total of 6.1 grams quinine *l*-glycerate melting at 174°, which proves very clearly that *dl*-glyceric acid was the main component of these gums. It is also clear from the above data that the separation of *dl*-glyceric acid from the two C_4 acids, *d*-erythronic and *l*-threonic, by means of strychnine, is not sharp but that mixed crystals of all of these components separate out from absolute alcohol. I have proved in an independent experiment that pure *dl*-glyceric acid gives with strychnine a low-melting (112° to 125°) crystalline salt which comes out to a very limited extent only from absolute alcohol, in which it is very soluble.

In conclusion, attention is drawn to the fact that I succeeded in proving definitely the nature of a far smaller proportion of the nonvolatile hydroxy acids formed by the action of air on an alkaline solution of *d*-glucose as compared with hydrogen peroxide. This is due mainly to the fact that in the former case relatively far greater amounts of *dl*-glyceric and optically active trihydroxybutyric acids are formed in proportion to the *d*-arabonic acid. I succeeded, for example, in obtaining only 17.75 grams of crude *d*-arabonic phenylhydrazide from 36 grams gums in the case of air, whereas I obtained 72.15 grams similar hydrazides from 83 grams of nonvolatile gums in the hydrogen peroxide experiment. The specific rotation of the original nonvolatile hydroxy acids was therefore also found to be far more strongly dextro in the latter case. Furthermore, experience has shown that it is impossible to remove more than a very small amount of *d*-arabonic lactone by the phenylhydrazine treatment of gummy mixtures whose specific rotation is not greater than 30°.0. It would therefore have been far more advantageous had I first resolved my gummy lactone mixtures, whose specific rotations varied from 5° to 30°, by digestion with solvents (small quantities of ethyl acetate and subsequently much ether, etc.) into gummy fractions which were levorotatory and into dextrorotatory gums whose specific rotation was at least 40°, before further treatment with reagents.

To Dr. Nef, whose constant help alone made this work possible, I extend my heartiest thanks.

THE ACTION OF LIGHT ON ESTERS OF α-CYANOCINNAMYLIDENACETIC ACID. II

By Marie Reimer and Eleanor Keller

In a previous paper[1] it was shown that the action of light on the methyl and ethyl esters of α-cyanocinnamylidenacetic acid, exposed without solvent, is to cause polymerization of these compounds. This work has now been extended to a study of a number of esters of this acid with two purposes in view: To compare the reactions of the compounds when exposed to the light in the dry condition and in solution, and to obtain, if possible, geometrically isomeric esters and study their reactions.

In many cases substances containing an ethylene linkage, when exposed in solution to the light, are isomerized to an unstable form.[2] Exposed without solvent, the reaction is usually polymerization or oxidation or both. That the same substance may behave very differently according to conditions of exposure is shown in the case of cinnamic acid which, without solvent, is polymerized in the light to α-truxillic acid,[3] but, in solution in benzene, is isomerized to isocinnamic acid.[4] The behavior in the sunlight of α-cyanocinnamylidenacetic esters, also, has been found to depend on these conditions of exposure. The methyl, ethyl, propyl, isopropyl and isobutyl esters were investigated. Without solvent all of the esters polymerize to a dimeric form. This reaction is practically quantitative except in the case of the stable ethyl ester which is considerably oxidized. In solution in alcohol, polymerization occurs in the case of the methyl ester only; all of the esters are decomposed slightly, oxidation taking place; and the ethyl ester is isomerized to an unstable form. In benzene solution the reactions are the same, except in the case of the methyl ester, which does not polymerize.

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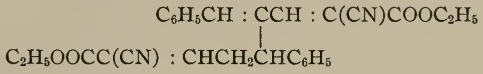
[1] This Journal, **45**, 417.

[2] Stoermer: Ber. d. chem. Ges., **42**, 4865; **44**, 637.

[3] Rüber: *Ibid.*, **35**, 2908.

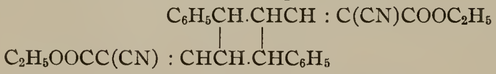
[4] Stoermer: *Ibid.*, **44**, 666.

Of chief interest in the behavior of these esters is the fact that the geometrical isomers studied react differently on exposure to the light. Isomeric ethyl and isobutyl esters were prepared. The stable ethyl cyanocinnamylidenacetate, when exposed in the dry condition, is partially oxidized and partially polymerized, slowly, to form a dimeric product, melting at 166°, to which has been ascribed the formula



$$\begin{array}{l}C_6H_5CH : CCH : C(CN)COOC_2H_5\\ |\\ C_2H_5OOCC(CN) : CHCH_2CHC_6H_5\end{array}$$

deduced from a study of the reactions of the compound as described in the previous paper. Exposed in solution in alcohol or benzene oxidation also occurs; more than 50 per cent. of the ester, however, is isomerized to an unstable form. The unstable ethyl cyanocinnamylidenacetate, exposed without solvent, is not oxidized but polymerized rapidly and quantitatively to the tetramethylene compound



$$\begin{array}{l}C_6H_5CH.CHCH : C(CN)COOC_2H_5\\ |\quad|\\ C_2H_5OOCC(CN) : CHCH.CHC_6H_5\end{array}$$

melting at 128°, which was previously described.

In solution the unstable form is affected by light less rapidly than the stable form. The compound is oxidized slightly, but no isomerization could be detected.

Exposed without solvent, then, one of these esters is oxidized, the other is not; both polymerize to give products not identical but structurally isomeric. In solution the stable ester is isomerized to the unstable form but the reverse of this reaction has not been found to take place.

The differences between the reactions of the two isobutyl esters is not so marked. Without solvent, the stable ester polymerizes more rapidly than its isomer to form a stable tetramethylene compound, the structure of which is proved by its oxidation to α-truxillic acid. The unstable ester polymerizes slowly to give a compound which breaks down rapidly in hot alcohol and which, on oxidation, gives a mixture of products from which no pure compound has been obtained. This polymer differs, therefore, in structure from that obtained from the stable form. Exposed to the light in solution, the unstable ester is decomposed more rapidly than the stable form. Neither ester has been found to isomerize.

Since the difference in the behavior of these isomeric esters is undoubtedly due to their difference in spatial configuration, it is quite probable that the action of light on other ethylenic compounds is determined, not only by the chemical influence of the groups present and the structure, but also, to a certain extent at least, by the spatial configuration of the molecule. The anomalous behavior of cinnamylidene compounds, on exposure, recently pointed out by Stobbe,[1] may find an explanation in the assumption that in this series compounds of different configuration, which, therefore, react differently in the light, are compared.

A satisfactory comparison, then, of the action of light on a series of unsaturated compounds can be made only when the conditions of the reactions are the same in all cases and when as many isomeric forms as possible have been investigated.

The behavior of the polymeric compounds formed from these esters, when exposed to the light in solution, has also been investigated for the purpose of testing Stewart's theory that the mechanism of the isomerization of unsaturated compounds in the light is the formation, from two molecules of the compound exposed, of a molecule of a tetramethylene polymer, which immediately breaks down in a different way from that in which it was formed to give two molecules of an isomeric form of the original compound.[2] The objection to this theory has been that tetramethylene compounds are not unstable and do not thus break down in solution. The polymeric compounds formed from the esters here described do, however, decompose in alcoholic solution when heated or when exposed to the light.

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[1] Ber. d. chem. Ges., **45**, 3396.

[2] P. Chem. Soc. (London), **21**, 73.

The yellow solutions were found to contain, however, no isomeric form of the esters but only decomposition products. The polymer formed from the stable ethyl ester, which breaks down even more readily than the tetramethylene polymers, gives only decomposition products while the stable ethyl ester itself isomerizes to give a 60 per cent. yield of the unstable ester. Although these polymeric compounds are decomposed in solution there is, then, no evidence of the formation of isomers. A more plausible explanation of the isomerization reaction would seem to be that there is formed an intermediate addition compound, much less stable than any isolated, perhaps by some such reaction as that suggested by Emil Fischer to account for the Walden inversion,[1] which breaks down to give the unstable form of the original compound.

The action of light on other cinnamylidene esters is in progress in this laboratory.

EXPERIMENTAL

The finely powdered esters were exposed to the sunlight in ten-gram lots spread out over glass plates twelve inches square. The temperature of exposure varied from 28° to 35° C. When a solvent was used the saturated solution was exposed in Erlenmeyer flasks. No catalytic agent was used in any reaction.

Methyl α-Cyanocinnamylidenacetate.—The preparation of this ester and the rapid formation of the tetramethylene polymer when it is exposed without solvent to bright sunlight were described in the previous paper. Dissolved in methyl alcohol, the ester rapidly loses its yellow color, the white polymeric compound separating out after a few days. After two months' exposure more than one-half of the ester had separated out in polymeric form. The very pale yellow solution left, on evaporation, more of the polymer and a trace of yellow oil smelling of benzaldehyde. Oxidation had therefore taken place as well as polymerization. In benzene solution, after one month's exposure, no polymer was formed; a considerable quantity of oxidation product and the unchanged ester were left on evaporation of the solvent. Since no isomeric form of the ester was obtained by exposure in solution, attempts were made to obtain an isomer by preparation of the methyl ester from the stable ethyl ester according to the method of Pfannl.[1] Ten grams of ethyl ester were suspended in 100 grams of methyl alcohol, potassium methylate added, one molecule for each molecule of the ethyl ester used, and the mixture shaken until the ethyl ester had all gone into solution. Almost immediately a nearly quantitative yield of methyl ester separated from the alcoholic solution. It was identical with the ester prepared by the usual methods. The reaction was repeated several times under varying conditions of temperature and concentration, but always with the same results.

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[1] Ann. Chem. (Liebig), **381**, 123.

The tetramethylene polymer was dissolved in methyl alcohol and exposed to bright sunlight. After several weeks a faint yellow color appeared. This color did not increase appreciably after six months. The alcoholic solutions, after spontaneous evaporation, left a trace of yellow oil, due evidently to oxidation, as benzaldehyde was present. There was no monomeric ester in the solution.

Ethyl α-Cyanocinnamylidenacetate (*Stable Form*).—This ester, melting at 113°, may be prepared quantitatively from the acid by heating the latter with a 3 per cent. solution of hydrochloric acid in ethyl alcohol or by the Claisen condensation of ethyl cyanoacetate with cinnamic aldehyde. On exposure to the light in the dry condition, oxidation takes place and 50 per cent. of the ester is polymerized to the compound melting at 166°, as previously described. Exposed in solution in ethyl alcohol, oxidation and isomerization occur. Eight grams of ester were dissolved in one liter of absolute alcohol and exposed to sunlight for six weeks. The alcohol was then allowed to evaporate spontaneously. The product was a dark oil with a strong nutty odor, filled with long needle-shaped crystals. The mixture was washed several times with small quantities of cold alcohol until the oil was all dissolved. From this alcoholic solution two grams of the original stable ester gradually separated. The crystals not dissolved by the cold alcohol were dissolved in the least possible quantity of boiling alcohol.

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[1] Monats. Chem., 31, 301.

From this solution 5 grams of unstable ester separated. In solution in benzene the results are the same. In bright sunlight over 60 per cent. was isomerized in 4–5 weeks. In subdued light the oxidation proceeds more rapidly than the isomerization so that little or no isomer was obtained in cases where the solution was not exposed to the bright sunlight.

The polymeric product is readily decomposed in alcoholic solution. On warming, the solution becomes yellow and then red. In the sunlight the reaction is not so rapid. Two grams of the ester were suspended in 100 cc. of ethyl alcohol and exposed. After two days a faint yellow color was discernible, the color rapidly increasing until the solution was a brilliant yellow. After 8 weeks the yellow solution was poured off and the alcohol evaporated. The only crystalline product separating was a little of the original polymer. The yellow color was that of an oil, having a characteristic nutty odor, in which benzaldehyde was present. Even in the dark the alcoholic solution of the polymer is decomposed slightly to form this yellow oil. Three grams of the polymer were suspended in two liters of alcohol and allowed to stand 1 month in the dark. The alcoholic solution, which had become a bright yellow, was then poured into several liters of water and the whole extracted with ether. On evaporation, the ether deposited a small quantity of yellow oil and a white crystalline compound, which separated from hot alcohol in fine, soft, colorless needles, melting at 182°. The quantity of this substance obtained in repeated experiments was not enough for analysis. As it is colorless, it may be an isomeric form of the polymer melting at 166°, the monomeric esters having invariably a yellow color.

Exposed in benzene solution, the reaction in the sunlight is the same as with alcohol. In the dark and on boiling the solution was not changed. In chloroform the decomposition in the light is extremely slow and in ether no change takes place. In no case was there any evidence of an isomeric form of the original ethyl ester.

Ethyl α-Cyanocinnamylidenacetate (*Unstable Form*).—This ester, melting at 113°, was first prepared by the reaction of potassium ethylate on an ethyl alcohol solution of the methyl ester, as described in the previous paper. It can be prepared more conveniently by exposure to the bright sunlight of the stable ester in alcoholic or benzene solution. The substance is very readily soluble in benzene, chloroform and acetone, fairly soluble in ether, insoluble in ligroin. It is much less soluble in methyl and ethyl alcohols than the stable form and can, therefore, be separated from the latter by fractional crystallization from alcohol. It separates from absolute alcohol in broad, flat, straw-colored needles, very different in appearance from the fine branching yellow needles of the stable ester.

Analysis:

0.1998 gram substance gave 0.5443 gram CO_2 and 0.1137 gram H_2O.

	Calculated for $C_{14}H_{13}O_2N$	Found
C	74.00	74.27
H	5.72	6.32

Exposed to the sunlight in the dry condition, the ester polymerizes rapidly and completely to the tetramethylene compound, melting at 128°, previously described.

In solution in alcohol exposure to the sunlight causes a little deeper yellow color to appear after a few days. This is evidently due to the formation of the oily decomposition product which was left, together with unchanged ester, on evaporation of the solvent. Although there is no evidence of isomerization of this ester, it is quite possible that such a reaction does take place, the stable ester thus formed being decomposed as rapidly as it is formed.

The tetramethylene polymer exposed to the sunlight in solution in alcohol is decomposed with extreme slowness. After exposure for 10 weeks a very faint yellow color was noticeable. The only products obtained from the solution were the unchanged polymer and the oily decomposition product.

Propyl Cyanocinnamylidenacetate.—The compound was prepared by the Claisen condensation of cinnamic aldehyde with propyl cyanoacetate; from a solution of cyanocinnamylidenacetic acid in propyl alcohol saturated with hydrochloric acid; and by dissolving ethyl α-cyanocinnamylidenacetate in propyl alcohol and treating with one molecule of potassium propylate.

The same ester, separating from propyl alcohol in long, flat, orange-yellow crystals, melting at 107°, was obtained in all cases. It is very readily soluble in acetone, benzene and chloroform, readily soluble in ether, very slightly soluble in ligroin. It is fairly soluble in cold methyl, ethyl and propyl alcohols, from concentrated hot solutions in which it crystallizes readily.

Analysis:

0.1990 gram substance gave 0.5429 gram CO_2 and 0.1158 gram H_2O.

	Calculated for $C_{15}H_{15}O_2N$	Found
C	74.69	74.40
H	6.22	6.53

Molecular weight determined in boiling benzene ($K = 26.1$):

Grams solvent	Gram substance	Rise in boiling point	Molecular weight
51.25	0.1604	0°.034	240
51.25	0.4499	0°.093	246
		Calculated for $C_{15}H_{15}O_2N$,	241

In diffused daylight the ester slowly loses color until a perfectly white product is formed. In bright sunlight the reaction is very rapid. In an hour the substance becomes a clear yellow, pasty mass which rapidly loses color, white crystals gradually separating. The paste contains no oxidation product, as a quantitative yield of polymer was obtained, but is evidently a mixture of the mono- and polymeric forms. When treated with cold alcohol the mass solidifies to a pure white compound which separates from boiling propyl alcohol in fine white needles melting at 107°–108°. It is very slightly soluble in cold alcohols, readily soluble in hot alcohols, benzene, acetone and chloroform, slightly soluble in ether, insoluble in ligroin.

Analysis:

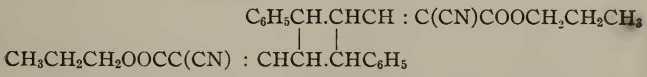
0.2004 gram substance gave 0.5500 gram CO_2 and 0.1184 gram H_2O.

	Calculated for $C_{30}H_{30}O_4N_2$	Found
C	74.69	74.85
H	6.22	6.56

Molecular weight determined in boiling benzene ($K = 26.1$):

Grams solvent	Gram substance	Rise in boiling point	Molecular weight
41.19	0.2610	0°.034	486
41.19	0.4418	0°.054	518
	Calculated for $C_{30}H_{30}O_4N_2$,		482

The structure of this dimeric compound was determined by oxidation. Two grams were dissolved in acetone, the solution cooled and potassium permanganate added as long as decolorizarion took place. The excess of oxidizing agent was then decolorized by sulphur dioxide, the oxides of manganese filtered out and extracted repeatedly with hot water. From the aqueous solution hydrochloric acid precipitated α-truxillic acid which melted at 274° when mixed with a sample of α-truxillic acid from another source. Benzoic and oxalic acids were obtained from the filtrate. These results prove the compound to be dipropyltetramethylenebismethylenecyanoacetate:



$$\begin{array}{r} C_6H_5CH.CHCH : C(CN)COOCH_2CH_2CH_3 \\ CH_3CH_2CH_2OOCC(CN) : CHCH.CHC_6H_5 \end{array}$$

The reaction is then analogous to that of the methyl and unstable ethyl esters.

In solution in alcohol the ester is only very slowly changed on exposure to the sunlight. After two months almost the whole amount of original ester crystallized out on evaporation of the solvent. A trace of decomposition product, but no polymer nor isomer, was present.

The polymeric product also decomposes on exposure in alcoholic or benzene solution with extreme slowness to give only decomposition products.

Isopropyl Cyanocinnamylidenacetate.—The ester was prepared from the corresponding acid and by the Claisen condensation as with the other esters. It separates from hot isopropyl alcohol in clear lemon-yellow plates melting at 111°–112°. It is readily soluble in benzene, chloroform, acetone and hot alcohols, fairly soluble in cold alcohols, ether and ligroin.

Analysis:

0.2012 gram substance gave 0.5511 gram CO_2 and 0.1203 gram H_2O.

	Calculated for $C_{15}H_{15}O_2N$	Found
C	74.69	74.70
H	6.22	6.70

Molecular weight determined in boiling benzene ($K = 26.1$):

Grams solvent	Gram substance	Rise in boiling point	Molecular weight
54.44	0.2265	0°.044	246
54.44	0.5443	0°.110	237
		Calculated for $C_{15}H_{15}O_2N$,	241

On exposure to the sunlight without solvent the ester rapidly loses color and becomes pasty. After 4–5 days the whole is a clear, colorless mass which crumbles to a white solid on treatment with cold alcohol. This solid separates from hot alcohol in stiff needles, colorless after several recrystallizations, melting at 136°. The compound is not readily soluble in cold alcohols nor in boiling ether, readily soluble in boiling alcohols, chloroform and benzene, fairly soluble in acetone, insoluble in ligroin.

Analysis:

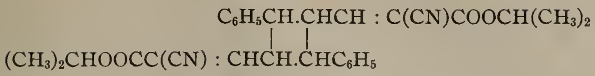
0.2234 gram substance gave 0.6137 gram CO_2 and 0.1281 gram H_2O.

	Calculated for $C_{30}H_{30}O_4N_2$	Found
C	74.69	74.87
H	6.22	6.37

Molecular weight determined in boiling benzene ($K = 26.1$):

Grams solvent	Gram substance	Rise in boiling point	Molecular weight
49.59	0.2938	0°.033	470
49.59	0.5644	0°.062	481
		Calculated for $C_{30}H_{30}O_4N$,	482

On oxidation in acetone solution with potassium permanganate the product was α-truxillic acid as in the case of the propyl ester. The compound is, therefore, diisopropyl tetramethylenebismethylenecyanoacetate:



$$\begin{array}{r} C_6H_5CH.CHCH : C(CN)COOCH(CH_3)_2 \\ | \quad\ \ | \qquad\qquad\qquad\qquad\qquad\quad \\ (CH_3)_2CHOOCC(CN) : CHCH.CHC_6H_5 \qquad\qquad\qquad\qquad \end{array}$$

On exposure in solution in alcohol the monomeric ester is decomposed more rapidly than the propyl ester. After exposure for several months a considerable quantity of yellow oil, smelling strongly of benzaldehyde, was deposited from the solution, together with a small amount of unchanged ester. No isomer nor polymer was present.

The polymer in alcoholic solution very gradually breaks down on exposure to the light to give a pale yellow solution. The color here is due, as in the other reactions, to a small quantity of decomposition product which separates as a yellow oil on evaporation of the alcohol.

Isobutyl Cyanocinnamylidenacetate (*Stable Form*).—Ten grams of α-cyanocinnamylidenacetic acid were dissolved in 130 cc. of isobutyl alcohol saturated with hydrochloric acid and the mixture allowed to stand overnight. The crystalline product was then filtered and recrystallized from hot isobutyl alcohol. The substance separates in lemon-yellow plates, melting at 114°. It is fairly soluble in cold methyl, ethyl and isobutyl alcohols and ether, readily soluble in hot alcohols and acetone, very soluble in benzene and chloroform.

Analysis:

0.1979 gram substance gave 0.5468 gram CO_2 and 0.1245 gram H_2O.

	Calculated for $C_{16}H_{17}O_2N$	Found
C	75.29	75.35
H	6.66	7.05

Molecular weight determined in boiling benzene (K = 26.1):

Grams solvent	Gram substance	Rise in boiling point	Molecular weight
46.04	0.1930	0°.043	254
		Calculated for $C_{16}H_{17}O_2N$,	255

On exposure to sunlight the ester rapidly forms an oil from which colorless crystals begin to separate in 2–3 hours. If the light is very bright, but little of the oil is formed, the substance rapidly decolorizing to a white solid mass. After two days' exposure the product was crystallized from alsolute alcohol. It separates in brilliantly shining white needles, melting at 123°. The substance is readily soluble in acetone, benzene, chloroform and hot alcohols, very slightly soluble in boiling ether and ligroin.

Analysis:

0.2020 gram substance gave 0.5604 gram CO_2 and 0.1192 gram H_2O.

	Calculated for $C_{32}H_{34}O_4N_2$	Found
C	75.29	75.66
H	6.66	6.54

Molecular weight determined in boiling benzene ($K = 26.1$):

Grams solvent	Gram substance	Rise in boiling point	Molecular weight
42.26	0.1884	0°.023	505
		Calculated for $C_{32}H_{34}O_4N_2$,	510

On treatment in acetone solution with potassium permanganate, the compound is rapidly oxidized to give an almost quantitative yield of α-truxillic acid. The compound is, therefore, the tetramethylene polymer.

In solution in alcohol isobutyl cyanocinnamylidenacetate slowly decomposes on exposure. After one month the alcohol was allowed to evaporate off. A very small quantity of yellow oil, smelling strongly of benzaldehyde, was formed; the bulk of the ester crystallized out unchanged.

The polymer, dissolved in alcohol, also decomposed very slowly on exposure to give a pale yellow solution. An oil, having the characteristic nutty odor of the decomposition products already described, was the only substance isolated aside from the unchanged polymer.

Isobutyl α-Cyanocinnamylidenacetate (*Unstable Form*).—This ester was prepared by the Claisen condensation from cinnamic aldehyde and isobutyl cyanoacetate. It crystallizes from hot isobutyl alcohol in shining yellow plates melting at 110°–111°. It is readily soluble in hot alcohols, ether, chloroform, acetone and benzene, slightly soluble in ligroin.

Analysis:

0.1994 gram substance gave 0.5491 gram CO_2 and 0.1239 gram H_2O.

	Calculated for $C_{16}H_{17}O_2N$	Found
C	75.29	75.10
H	6.66	6.96

Molecular weight determined in boiling benzene ($K = 26.1$):

Grams solvent	Gram substance	Rise in boiling point	Molecular weight
48.82	0.1802	0°.040	241
48.82	0.3963	0°.088	241
	Calculated for $C_{16}H_{17}O_2N$,		255

The ester is isomeric with the one just described. On boiling in isobutyl alcohol saturated with hydrochloric acid it gradually changes to the higher-melting isomer. It may, therefore, be considered the unstable form. As the melting points of the two esters lie very close together and as they do not differ in appearance and but very slightly in solubility, they may most readily be distinguished by exposing small quantities of each to the light and comparing their behavior and the products formed. The unstable ester on exposure gradually forms a clear pasty product, readily soluble in the common organic solvents. After exposure for two weeks the paste has hardened to a clear mass which crumbles to a white powder when treated with cold alcohol. Crystallized from boiling absolute alcohol, the compound separates in fine white needles melting from 114°–115°. The alcohol solution from which the compound is crystallized becomes a dark, reddish yellow, showing considerable decomposition of the substance on heating in alcohol, as is the case with the polymer from the stable ethyl ester.

The substance is slightly soluble in cold alcohols, readily soluble in hot methyl, ethyl and isobutyl alcohols and in benzene, acetone and chloroform.

Analysis:

0.1886 gram substance gave 0.5194 gram CO_2 and 0.1180 gram H_2O.

	Calculated for $C_{32}H_{34}O_4N_2$	Found
C	75.29	75.18
H	6.66	6.41

Molecular weight determined in boiling benzene ($K = 26.1$):

Grams solvent	Gram substance	Rise in boiling point	Molecular weight
50.73	0.5658	0°.057	510
	Calculated for $C_{32}H_{34}O_4N_2$,		510

This substance is then a dimeric form of the unstable isobutyl ester, isomeric with the higher-melting polymer obtained by exposure of the stable isobutyl ester.

The oxidation of the two polymeric compounds was carried out side by side for purposes of comparison. Two grams of each polymer were dissolved in 50 cc. of acetone and treated slowly with 3 grams of potassium permanganate dissolved in 100 cc. of acetone. The mixtures were kept at 0° throughout the reaction. After complete decolorization of the permanganate the solutions were filtered and the oxides of manganese repeatedly extracted with boiling water. From the aqueous solution obtained by oxidation of the high-melting polymer hydrochloric acid precipitated an almost quantitative yield (1.0 gram) of α-truxillic acid as a pale yellow flocculent precipitate. From the aqueous solution obtained by oxidation of the low-melting polymer, hydrochloric acid precipitated about 0.1 gram of a pasty substance, which gradually solidified. After repeated crystallizations from alcohol this melted at 250°–270°. It behaved somewhat like α-truxillic acid but could not be identified as that acid. The aqueous solution filtered from this solid was extracted repeatedly with ether. On evaporation the ether deposited a solid which was crystallized from boiling water. It separates in white clumps melting at 210°–250° with decomposition. The substance is very soluble in the usual organic solvents. It has not yet been possible to obtain it in condition pure enough for analysis. It has none of the characteristics of the acid formed by oxidation of the polymer from the stable ethyl ester and, therefore, this unstable isobutyl polymer must differ in structure from any as yet obtained from these esters.

Exposed in solution in alcohol, the unstable isobutyl ester decomposes more readily than the stable ester. No isomeric nor polymeric form was found in the solution.

The polymeric product also decomposes more readily than that from the stable ester when exposed in alcoholic solution. Only the yellow oil, containing benzaldehyde, was isolated from the solution.

Chemical Laboratory
Barnard College
June, 1913

REPORT

THE EVOLUTION OF AVOGADRO'S THEORY[1]

Avogadro put forward his celebrated hypothesis in 1811. In 1814 Ampère announced the same hypothesis. But it required more than half a century to bring chemists generally to its acceptance. Now it is a fundamental chemical and physical theory.

In 1804 Humboldt visited Berthollet and met Gay-Lussac who, though only 25 years old, had already distinguished himself, especially by the discovery of the law of expansion of gases. Humboldt, wishing to improve the method of analyzing air, invited Gay-Lussac to determine the best method of estimating oxygen in the air. It was necessary to determine accurately in what volumetric proportion oxygen unites with hydrogen. They found that 1 volume of oxygen combines with 2 volumes of hydrogen. They published the result in 1804. Later Gay-Lussac (1808) announced his law of volumes. He did not suggest any hypothesis by way of explanation.

Avogadro, in 1811, began his now-celebrated article by referring to the results of Gay-Lussac and then says:

"Il faut donc admettre qu'il y a aussi des rapports très simples entre les volumes des substances gazeuses et le nombre des molécules simples ou composées qui les forme. L'hypothèse qui se présente la première à cet égard et qui parait même la seule admissible, est de supposer que le nombre des molécules intégrantes dans les gaz quelconques est toujours le même à volume égal ou est toujours proportionnel aux volumes." . . .

"En partant de cette hypothèse on voit qu'on a le moyen de déterminer très aisément les masses relatives des molécules des corps qu'on peut avoir à l'état gazeux."

Further referring to the molecules of elements, he says:

"Les molécules constituantes d'un gaz simple quelconque, c'est-à-dire celles qui s'y tiennent à une distance telle à ne pouvoir exercer leur action mutuelle, ne sont pas formées d'un seule molécule élémentaire mais résultent d'un certain nombre de ces molécules réunies en une seule par attraction."

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[1] Abstract of an article entitled "Der Entwicklungsgang der Avogadroschen Theorie," by C. Graebe, Journal für praktische Chemie, N. F., **87**, 145–208 (February, 1913).

The *molécules constituantes* and *molécules intégrantes* of Avogadro were our molecules, but by *molécules constituantes* he means the molecules of elements and by *molécules intégrantes* he generally means the molecules of compounds, but also molecules of all substances, and later the molecules of elements. The word atom does not occur in Avogadro's articles that appeared from 1811 to 1814.

Graebe considers the recognition of the complexity of the molecules of the elements the greatest scientific contribution of Avogadro. This was entirely new. Dalton had distinctly denied that the same number of smallest particles is contained in the same volume of all gases.

In 1814 Avogadro says:

"Les expériences et analyses qui ont été publiées depuis par plusieurs physiciens et chimistes, et en particulier par MM. Gay-Lussac, Davy et Berzelius, etc., nous permettent maintenant d'étendre nos principes à d'autres substances, sur lesquelles il nous était resté des doutes, ou dont nous n'avons pas parlé."

Attempts by Avogadro to apply the hypothesis to substances which could not be vaporized led to confusion. This made chemists hesitate to accept the hypothesis. Then, too, Avogadro made no experiments.

In 1821 Avogadro published two more articles, one dealing with results which had been obtained by Berzelius, and the other with the question as to the molecular weights of alcohol and ether. These two articles remained unknown to chemists until 1901, when Guareschi called attention to them. It is probable that Berzelius never saw them. Avogadro never tried to impress his views on other chemists. He was very modest. This fact probably explains why he never took exception to the statements of Dumas and Gaudin in regard to the historical development of his hypothesis.

In 1814 appeared the "Lettre de M. Ampère à M. le comte Berthollet sur la détermination des proportions dans lesquelles les corps se combinent d'après le nombre et la disposition respective des molécules dont leurs particules intégrantes sont composées."

By *molécule* Ampère meant our *atom*, and by *particule* our molecule.

Like Avogadro, Ampère starts with Gay-Lussac's law:

"Vous savez que depuis longtemps l'importante découverte de M. Gay-Lussac sur les proportions simples qu'on observe entre les volumes d'un gaz composé et ceux des gaz composants m'a fait naître l'idée d'une théorie qui explique les faits découverts par cet habile chimiste et les faits analogues observés depuis." . . . "Les particules de tous les gaz, soit simples, soit composées, sont placées à la même distance les unes des autres. Le nombre des particules est dans cette supposition, proportionnel au volume de gaz."

In a footnote he adds: "Depuis la rédaction de mon Mémoire j'ai appris que M. Avogadro avait fait de cette dernière idée la base d'un travail sur les proportions des éléments dans leur combinaisons chimiques."

Ampère's views in regard to the divisibility of the molecules of the elements are the same as Avogadro's.

"Le gaz nitreux (nitric oxide) contenant, par exemple, la moitié de son volume en oxygène et la moitie en azote, il s'ensuit qu'une particule de gaz nitreux est formée par la réunion de la moitié d'une particule d'oxygène et la moitié d'une particule d'azote."

Avogadro and Ampère differ widely in regard to the number of atoms in the molecules of the elements. These complications are probably responsible for the fact that this article was not reproduced in any of the other journals. The greater part of the article is an attempt to determine how the atoms can combine with one another according to the fundamental crystalline forms.

Ampère returned to the subject only once afterwards—eighteen years later. In the later article he defines atom and molecule as they are now defined. He was the first to do this.

From 1811 to 1826 the subject received no further attention. There was not even a reference to the publications of Avogadro and Ampère.

In 1813 Berzelius held that the atomic weights are proportional to the specific gravities in gaseous condition, but he did not extend this idea to compounds and never held that equal volumes of all bodies in gaseous condition contain the same number of molecules.

In 1826 appeared Dumas' *Mémoire sur quelques points de la Théorie atomique.* He refers to Ampère but only secondarily to Avogadro. After this the hypothesis was called Ampère's hypothesis until Cannizzaro set matters straight in 1858. At the end of his article Dumas says:

"Nous sommes bien eloignés de l'époque où la chimie moléculaire pourra se diriger par des règles certaines, malgré les avantages immenses que cette partie de la philosophie naturelle a retirés des travaux de MM. Gay-Lussac, Berzelius, Dulong and Petit, Mitscherlich, ainsi que les vues théoriques de MM. Ampère et Avogadro."

Dumas did not distinguish sharply between atom and molecule. He used the expression "half atom" which led Berzelius to remark:

"Ehemals war es gewöhnlich, dass man eine Hypothese, sobald sie ad absurdum führte, als widerlegt zu betrachten."

In 1832 Dumas found himself in trouble on account of the peculiar results obtained in determining the vapor densities of mercury, phosphorus and sulphur. He halved the atomic weight of mercury and doubled that of phosphorus.

In 1833 Berzelius, in consequence of Dumas' results, abandoned the view that equal volumes of elements in gaseous condition contain the same number of atoms.

In 1833 Gaudin advanced ideas essentially the same as those of Avogadro and Ampère, but he did not mention Avogadro. He held that the molecule of mercury is monatomic, that of phosphorus tetratomic, and that of sulphur hexatomic.

Gay-Lussac and Becquerel made a report to the French Academy upon Gaudin's memoir and in the report occurs this passage:

"Il fait voir que les molécules de vapeur de brome et d'iode sont biatomiques au moins, comme celle du chlore; celle de mercure monoatomique. Le phosphore à l'état de vapeur est tetratomique et la soufre hexatomique."

Berzelius reports in full upon this article in his Jahresbericht. He says: "Das Hauptaxiom ist der von Ampère aufgestellte Satz, dass in allen Gasen der Abstand zwischen den Atomen gleich ist."

Gaudin's article was long ignored or forgotten. In 1838, Avogadro mentions it but does not agree with the author as to the monatomicity, diatomicity, etc., of elementary molecules.

Gaudin's article was helpful in leading to the use of the words atom and molecule in the present sense. In 1858, Cannizzaro confessed his indebtedness to Gaudin in respect to this matter.

In the 30's of the last century vapor-density determinations were used more and more in organic chemistry to control analyses, but they were not taken as decisive. For example, in 1834, Liebig says: "Das specifische Gewicht des Alkoholdampfes kann nicht als Grund für seine Konstitution als ein Oxyd eines anderen Radikals angesehen werden."

Persoz, in 1839, in his "Introduction à l'étude de la chimie moléculaire" used these words:

"Le volume de vapeur que produisent les équivalents de chaque corps en partant de 100 g. d'oxygène pris pour unité est sensiblement égal à 70 litres de vapeur à 0° et 76 cm. de pression ou à un multiple de ce nombre par 2 ou 4, c'est-à-dire = 140 litres ou 280."

Later Berzelius found that the vapor of acetic acid has a specific gravity corresponding to 3 volumes, i. e., 70 × 3 = 210 liters.

In the first volume of his "Handbuch der Chemie" (1843), Gmelin did not specially treat of the hypothesis of Avogadro and Ampère, nor did he mention these investigators. He, however, says:

"Das Gesetz von Berzelius, dass einfache Stoffe im Gaszustand bei gleichem Volum eine gleiche Zahl von Atomen enthalten, ist bereits durch die Erfahrung widerlegt."

In Kopp's "History of Chemistry" (1843–47) no mention is made of Avogadro, and Ampère is referred to only in connection with ammonium and hydrofluoric acid, although Kopp deals fully with the treatise of Dumas on the atomic theory. He doesn't mention the distinction between molecule and atom.

Thirty years later, in his "Entwicklung der Chemie in der neueren Zeit," Kopp gives an explanation of the neglect of Avogadro's treatise. He says chemists were just beginning to familiarize themselves with the relation between the composition of compounds and the relative weights of the smallest particles of the constituents, and the distinction between two kinds of smallest particles seemed rather to complicate than to simplify matters. But still more was the neglect due to the fact that Avogadro put forward his theory without stating a single new fact. And Ampère, who had a high reputation as a mathematician, did not succeed in enlisting adherents to the new ideas.

It appears, indeed, that Ampère's treatises on the molecular hypothesis were not regarded as of much importance even by those who stood in closest relations to him.

At the beginning of the 40's the hypothesis that equal volumes of bodies in the gaseous condition contain an equal number of molecules had been entirely abandoned by chemists. Only Avogadro and Gaudin accepted it but without furnishing further evidence.

Gerhardt recognized its value for the determination of formulas and began a new epoch in the history of Avogadro's theory. The formulas then in use were very complicated. Gerhardt went back to the empirical formulas and found that by using what appeared to be the most reliable atomic weights most formulas must be halved. In 1843 he chose equivalents that gave the formulas HCl, H_2O, NH_3, CO_2, KCl, KHO, SO_4H_2. For the non-metals his atomic weights were the same as those of Berzelius but with the important difference that he did not assume any double atoms. For the metals his atomic weights were half those of Berzelius. Those of Gerhardt are the same as those now in use with the exception that those of the polyvalent metals are now twice as large as his.

Gerhardt found that the formulas adopted by him for organic compounds whose vapor densities had been determined all corresponded to 2 volumes (i. e., H_2) as is the case with H_2O, CO_2, ClH, and NH_3. In his "Précis de chimie organique" (1844–1845), he says:

"On dit alors que l'équivalent de la substance représente deux volumes de vapeur."

He applied this principle consistently. The only exception was perchloromethyl ether, $(CCl_3)_2O$, which gave a vapor density half as great as was expected. He assumed that it broke down into tetrachloromethane and carbonyl chloride:

$$(CCl_3)_2O = CCl_4 + COCl_2.$$

This was experimentally confirmed by de Soney in 1893.

Gerhardt did not extend his view to the elements. For him the words atom, equivalent, and volume were synonymous. He had not yet accepted the view that the molecules of the elements are divisible.

Laurent was the first to adopt the views of Gerhardt, but he distinguished sharply between atom and molecule, using these words as Ampère and Gaudin had 12 years before. In 1846 Laurent says: "L'atome de Gaudin représente la plus petite partie d'un corps simple qui puisse exister dans une combinaison. Ma molécule représenterait la plus petite quantité d'un corps simple qu'il faut employer pour opérer une combinaison, quantité qui est divisible en deux par l'acte même de la combinaison. Ainsi, Cl peut entrer dans une combinaison; mais pour faire celle-ci, il faut employer Cl_2. J'admets donc, avec M. Ampère, la double décomposition du chlore par hydrogène.

"Si, au lieu de prendre 1 volume pour quelque corps, 2 volumes pour d'autres et 4 volumes pour d'autres, comme ou le fait ordinairement; ou bien, si an lieu de prendre comme M. Gerhardt 1 volume pour les corps simples et 2 volumes pour les corps composés, nous représentons tous les corps, tant simples que composés, par 1 volume nous aurons une notation beaucoup plus régulière.—On a alors:

1 Molécule

Oxygène O_2 = 200.0 = 1 vol.
Hydrogène H_2 = 12.5 = 1 vol.
Eau H_2O = 112.5 = 1 vol.
Acide chlorhydrique HCl = 227.0 = 1 vol."

Laurent uses for the first time such equations as the following:

$$\mathrm{(HH) + (ClCl) = (HCl) + (HCl)}$$
$$\mathrm{(HH) + (HH) + (OO) = (HH)O + (HH)O.}$$

He also explains the nascent state in the same way as is customary at present.

In 1846, Favre and Silbermann, in studying heat changes in chemical processes, came to the same conclusions as Laurent in regard to complexity of elementary molecules. They found that more heat is evolved when carbon is burned in nitrous oxide than when carbon is burned in oxygen and gave the now commonly accepted explanation that more energy is required to separate the atoms of oxygen from each other than to separate the atom of oxygen from the two atoms of nitrogen contained in the molecule of nitrous oxide.

No notice was taken of these views until 1864, when Würtz in his "Lecons de philosophie chimique" said:

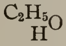
"Rappelous ici que MM. Favre et Silbermann, dans leurs recherches classiques sur les chaleurs produites par les combinaisons chimiques, ont émis les premiers l'idée que la molécule d'oxygène libre est formée de deux atomes."

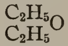
This is not correct, Avogadro was the first, but Favre and Silbermann furnished experimental evidence in favor of the idea.

Gerhardt and Laurent worked together earnestly, but they were not able to bring about the desired reform in the 40's. At this time nearly all chemists had given up the atomic weights of Berzelius and were using Gmelin's equivalents.

Gerhardt believed that ether was derived from 2 molecules of alcohol but furnished no evidence. Then came (1850) the important work of Williamson that led him to the conclusion that alcohol is water in which half of the hydrogen is replaced by hydrocarbon, and ether is water, in which both atoms of hydrogen are replaced by hydrocarbon,

$\begin{array}{l}\mathrm{H}\\\mathrm{H}\end{array}\mathrm{O}$


$\begin{array}{r}\mathrm{C_2H_5}\\\mathrm{H}\end{array}\mathrm{O}$


$\begin{array}{l}\mathrm{C_2H_5}\\\mathrm{C_2H_5}\end{array}\mathrm{O}$

Williamson abandons equivalents and adopts the atomic weights of Gerhardt. He does not, however, mention Avogadro or Ampère.

In the 50's more and more attention was given to the views of Gerhardt, but the abnormal vapor densities gave difficulty and prevented the general adoption of Avogadro's hypothesis.

Bineau (1838, 1839) determined the vapor densities of a number of ammonium salts and obtained smaller values than were to be expected—for ammonium chloride one-half; for ammonium carbamate one-third. He suggested that these salts may be decomposed by heat.

In 1846 Bineau found different densities for sulphuric acid at different temperatures and offered the same explanation as for ammonium salts.

These ideas were not fruitful at first. Chemists could not believe that hydrochloric acid and ammonia could exist side by side, or sulphuric anhydride and water. Even Gerhardt felt that this view was improbable.

Laurent in his "Méthode de Chimie" (1854) regards the abnormal vapor densities as exceptions. He defended Gerhardt's system of formulas and atomic weights warmly, and Gerhardt accepted Laurent's views regarding the molecules of the elements. Gerhardt even went so far as to speak of free chlorine as chloride of chlorine, and of hydrogen as hydride of hydrogen. He did not make use of the law of Dulong and Petit. All metals correspond to hydrogen; hence the formulas K_2O, Ca_2O, Hg_2O, etc.

In his "Traité de chimie organique" (1853–56) Gerhardt did not use his own atomic weights and only discussed them in the 4th volume. Being asked why he did not use the simpler system, he is said to have replied, "Dann hätte Niemand mein Buch gekauft."

Gerhardt died in 1856, two days before his 40th birthday. The 4th volume of his book was in manuscript and was published later. Laurent died in 1853, a year before his "Méthode de Chimie" appeared.

The work now devolved upon younger chemists—above all Cannizzaro and Kekulé. Both had spent some time in Paris, and later Kekulé went to London, where he became well acquainted with Williamson.

Mendeléeff early recognized the value of the new ideas. In his "Die Grundlagen der Chemie" (German edition, 1891) he speaks of the molecular hypothesis as the hypothesis of Avogadro and Gerhardt.

In 1857 Clausius used these words: "In dem ich nach einem gemeinsamen Gesetze für die Volumverhältnisse der Gase suchte, bin ich endlich bei folgender Ansicht, als der wahrscheinlichsten stehen geblieben, welche ich dem wissenschaftlichen Publikum wenigstens als eine Hypothese, die der weiteren Prüfung wert ist, glaube vorlegen zu dürfen. Ich nehme an, dass die Kraft, welche die Entstehung chemischen Verbindungen verursacht und wahrscheinlich in einer Art von Polarität der Atome besteht, auch schon in den einfachen

Stoffen wirksam ist, und dass auch in diesen mehrere Atome zu einem Molekül verbunden sind. Der einfachste und daher wahrscheinlichste Fall würde der sein, dass zwei Atome ein Molekül bilden."

Verdet called attention to the fact that these ideas of Clausius were not new, but that Laurent and Gerhardt had advanced similar views. Clausius afterwards acknowledged the justice of Verdet's criticism.

In 1857 appeared an important article by Sainte-Claire Deville entitled "Sur la dissociation ou la décomposition spontanée des corps sous l'influence de la chaleur." Deville always remained an opponent of Avogadro's theory but furnished some of the best evidence in its support.

Cannizzaro at once recognized the value of this evidence. He says:

"Ich glaube, dass es keine Ausnahme von dem allgemeinen Gesetz gibt, nach welchem gleiche Volum gasförmiger Körper eine gleiche Anzahl Moleküle enthalten, und dass die scheinbaren Anomalien bei einer strengen Prüfung verschwinden werden."

Kopp (1858), after the appearance of Deville's article, accepts the explanation of abnormal vapor densities suggested by it.

Kekulé (1858) also accepts the same explanation but he does not base his conclusions upon Deville's results. He is discussing Baeyer's discovery of the decomposition of cacodyl trichloride by heat.

Cannizzaro went farther than Kopp or Kekulé. He says Avogadro's hypothesis is in harmony with all facts. He expresses himself even more strongly in his "Sunto di un corso di filosofia chimica fatto nelle R. Università di Genova" (1858). This is the real turning point. He puts the main point very clearly.

"Ich glaube, dass die in dem letzten Jahren gemachten Fortschritte der Wissenschaft die Hypothese von Avogadro, Ampère und Dumas über die ähnliche Beschaffenheit im Gaszustand bestätigen, dass heist, dass gleiche Volum derselben, mögen sie einfach oder zusammengesetzt sein, eine gleiche Anzahl von Molekülen enthalten, aber nicht eine gleiche Anzahl von Atomen. . . . . In meiner ersten Vorlesung begann ich zu zeigen wie aus der Betrachtung der physikalischen Eigenschaften der Gase und des Gay-Lussac'schen Gesetzes über das Verhältniss des Volumens der Verbindungen und ihre Bestandtheile jene Hypothese fast von selbst entsprungen ist, welche zuerst von Avogadro und kurz nachher von Ampère verkündigt wurde."

This is the first statement to the effect that Avogadro was the first to suggest this hypothesis. The fact had been forgotten by his fellow-countrymen. It was not mentioned in an article which appeared in the Nuovo Cimento of Matteuci and Piria in 1856, at the time of Avogadro's death, nor in an article by Piria (1857), in which the author accepts the view of Gerhardt that the molecules of the elements consist of 2 atoms each.

Cannizzaro calls the molecular theory generally the hypothesis (sometimes the theory) of Avogadro and Ampère.

Cannizzaro proposed to select atomic weights of the metals to conform to the law of Dulong and Petit.

Kekulé, in his "Lehrbuch der organischen Chemie," the introduction to which appeared in 1859, bases his reasoning largely upon chemical considerations as did Gerhardt and Laurent. He reaches the conclusion "dass die chemischen Moleküle mit den physikalischen Gasmolekülen indentisch sind," and therefore that "gleiche Volume gasförmiger Körper eine gleiche Anzahl chemischer Moleküle enthalten."

Cannizzaro's "Sunto" was not republished in any journal, and the Jahresbericht gave only an inadequate account of it. Therefore it remained practically unknown. Then came the Congress of Chemists at Carlsruhe in 1860, which was due largely to the initiative of Kekulé. Here Cannizzaro played a leading rôle and made a strong impression. He proposed to adopt Gerhardt's system and to make the necessary changes in the atomic weights of a number of metals.

Kekulé and Strecker supported him but no decision was reached. One thing came out clearly—that Avogadro was the first to advance the hypothesis which was still frequently attributed to Ampère. At the close of the meetings Cannizzaro distributed reprints of his "Sunto." Later Lothar Meyer told of the effect upon himself of the careful study of this "Sunto." As he says: "Es fiel mir die Schuppen von den Augen, die Zweifel schwanden und das Gefühl ruhigster Sicherheit trat an ihre Stelle. Wenn ich einige Jahre später etwas für die Klärung der Sachlage und die Beruhigung der erhitzten Gemüter habe beitragen können, so ist das zu einem nicht un wesentlichen Teil der Schrift Cannizzaro's zu danken."

Kekulé in the last number (Lieferung) of the first volume of his "Lehrbuch" (1861) changed the atomic weights of mercury, zinc, tin, and lead. He doubled them as suggested by Cannizzaro.

Kopp, in the second edition of his "Theoretische Chemie" (1863), gives the newer views concerning molecular weights, atomic weights and equivalents according to Avogadro's hypothesis and the law of Dulong and Petit.

Lothar Meyer treats fully of Avogadro's hypothesis in his "Die modernen Theorien der Chemie" (1864). In the later editions he uses the expression Avogadro's rule.

Würtz, in his "Leçons de Philosophie chimique" (1864), speaks of the law of Ampère; in later publications of the law or theory of Avogadro and of Ampère; and finally he leaves Ampère's name off entirely.

In the second edition of his "Die modernen Theorien der Chemie" (1872) Lothar Meyer says:

"Seit die Schlussbetrachtungen zur ersten Auflage geschrieben wurden, hat die Entwicklung der theoretischen Chemie einen wesentlichen Schritt vowärts getan. Die damals noch bestrittenen oder doch nicht ausdrücklich anerkannten Hypothesen von Avogadro und von Dulong und Petit sind als die Grundlagen der Atomgewichtsbestimmung allgemein anerkannt worden; die Gmelinschen sog. Äquivalente sind aus der Literatur verschwunden."

Up to 1863 the "Jahresbericht" used only equivalents, then equivalents and atomic weights according to the author quoted; after 1873 only the new atomic weights.

In spite of all, the hypothesis of Avogadro still remained a subject of controversy, but the day was won. Würtz, in 1877, came to the defense, but felt that the hypothesis no longer needed a defender. He writes to van't Hoff in 1877:

"Avez-vons suivi dans le Compte rendu ma discussion avec Berthelot et Deville et n'est-il pas triste d'avoir à soutenir de pareils combats pour une cause gagnée depuis 20 ans?"

The discussion continued until 1880. Berthelot and Deville never accepted the hypothesis but they were without followers.

I. R.

REVIEWS

A Dictionary of Applied Chemistry. By Sir Edward Thorpe, C.B., LL.D., F.R.S., Emeritus Professor of Chemistry, Imperial College of Science and Technology, South Kensington, London, assisted by Eminent Contributors. Revised and enlarged edition in five volumes. Vol. IV, Oilstone to Soda Nitre. With illustrations. London, New York, Bombay and Calcutta: Longmans, Green & Co. 1913. pp. viii + 727. Price, $13.50.

Reviews of previous volumes of this new edition have appeared in these columns,[1] and it is very satisfying to find this fourth volume appearing with the promptness promised in the original prospectus, i. e., that the entire set should be complete in two years. To this volume forty-nine contributors have supplied the articles, some of which are quite long. About one hundred and fifty are new topics not found in the old edition, the more important being the following: Oxydases; Ozonides; Palm Kernel Oil; Palm Oil; Percarbonates; Perfumes (Synthetic); Phenylacetic Acid; Phenylglycine; Phytosterol; Pitchblende; Plant-Sprays; Polarimetry; Polonium; Propiolic Compounds; Propyl; Proteins; Ptomaines; Purpurogallin; Pyrazoline; Pyrimidines; Pyrites; Pyrometry; Pyronine Colors; Quebracho Colorado; Racemism; Radioactivity; Radium; Refractometer; Refrigerating and Ice-Making; Rhodinol; Rosinduline; Safrole; Samarium; Santalene; Santalol; Saponification; Scandium; Sewage; Silk, Artificial; Smoke and Smoke Prevention.

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[1] This Journal, **48**, 191, 259; **49**, 257.

About fifty articles from the old edition have been entirely rewritten and materially enlarged; among these may be noted: Oxalic Acid; Oxazine Coloring Matters; Oxygen; Ozone; Parchment Paper; Pepper; Persian Berries; Petroleum; Phenacetin; Phenanthrene; Photography; Phthalic Acid; Picric Acid; Pottery and Porcelain; Praseodymium; Primuline Derivatives; Purple of the Ancients; Pyrazolines; Pyrogallol; Quartz; Quinoline; Quinones; Quinone-oxime Dyes; Resins; Rubber; Rubidium; Rum; Rust; Salicylic Acid; Selenium; Silicon; Silver; Silvering.

The references cited in several cases show that the articles have been brought up to 1912. Many new references to mineral products used as raw materials, and to vegetable products such as fruits and drugs, have been included in this edition.

The topic of Oxygen is considered in two sections: the chemical methods of production, and the mechanical and electrical processes. Of the chemical methods, the manganese dioxide-potassium chlorate process and the Brin barium oxide process are still in use in a few places. But the mechanical process from liquid air, and the electrolysis of water, are now more important, although the electrolytic methods depend upon a market for the hydrogen, in order to compete with the liquid-air method. Both of these methods are well illustrated.

The industrial preparation and utilization of Ozone is well, though briefly, treated, and the several types of commercial ozonizers described in short paragraphs on each. The most important use for ozone is in purifying water for domestic purposes, and large scale installations at St. Petersburg, Florence, Nice and Philadelphia are cited. The cost of purifying water is also considered. The use of ozone for purifying the air in buildings and enclosed spaces, for bleaching various organic substances, and for sterilizing is also mentioned. Ozonides, the derivatives produced by the action of ozone on unsaturated organic compounds, fill three pages of text. Oxydases fill a page and a half, in which are several citations from the publications of Kastle and Loew in this country.

Synthetic Perfumes are treated in a readable article of about eight pages. It is stated that nearly all flower perfumes can be imitated, more or less successfully, but in the case of violet, and rose oil, the imitations do not approach the natural substance in fragrance. The relation between constitution and smell is discussed briefly. A list of substances used in compounding perfumes, with their constitutional formulae when known, their chemical properties, and methods of preparation or isolation from natural sources, is included. Also the constituents of the more important blends found in the market.

Under American Petroleum is found the first article, in this volume, by an American authority, Dr. S. P. Sadtler, of Philadelphia, who contributes a digest of the industry as at present conducted in this country. A longer article by Sir Boverton Redwood covers the industry as developed in other parts of the world, and especially a full discussion of the testing of petroleum oils.

Plant-Sprays are considered under the three classes, solids, liquids and gases, spraying being used in its widest sense as the application of these materials to plants to rid them of insects, fungoid parasites and other matters interfering with healthy growth. The methods of preparation and the application and properties of the more important sprays and washes are suitably discussed.

In the extensive article on Polarimetry, the qualitative and quantitative examination of optically active substances, the effect of asymmetric atoms on optical activity, Walden's inversion, the general relations of rotation and chemical constitution, the influence of changes of temperature and pressure on rotation, and the rotation of active salts in solution are fully treated. The optical principles of the Nicol prism and its various modifications, with descriptions of the polarimeters of Mitscherlich, Laurent, Lippich, and the modern Schmidt and Haensch instrument, are included.

In the article on Proteins, the labors of Emil Fischer and his students are well outlined. The reactions, physical properties, classification, separation and identification of the proteins are briefly considered. Then follow paragraphs upon the conjugated proteins and the hydrolysis of proteins by enzymes.

Pyrometery is set forth in an illustrated article of about eight pages. The various methods and instruments employed in high temperature determinations are well described; a bibliography of the subject is also included.

In the article on Quartz is a short paragraph upon its use for making fused silica ware, now so important in chemical industry. A somewhat more lengthy treatment of this subject is, however, found in the topic Silicon and a cross-reference here would be useful.

Quinones furnish one of the longest articles in this volume, profusely illustrated with structural formulae and equations, and interspersed with copious references to original literature.

The interesting developments of Radioactivity, beginning with Becquerel's work in 1896 and extending to the very recent papers by Rutherford and others, fill about ten pages.

Refractometers are illustrated by descriptions of the instruments of Pulfrich, of Abbe, the butter instrument, and the dipping instrument. The conditions essential for satisfactory work in investigations with these instruments are shown.

The article on Refrigerating and Ice-Making Machinery consists mainly of a theoretical consideration of the principles upon which are based the two general types of machines—those employing the expansion of compressed air and those depending on the abstraction of heat by evaporation of a volatile liquid. A number of industrial applications of refrigeration are cited, but few details of practice are given.

Rubber is the title which replaces *Caoutchouc* or *India-rubber* of the old edition. The constitution of rubber and its synthetic preparation by condensation of isoprene is referred to very briefly, but is admittedly not a commercial possibility as yet. The manufacture of rubber goods is described, with illustrations of some of the machinery.

Under Rust are outlined the various theories as to the causes and phenomena of the process, with reference to the older work of Crace Calvert and Crum Brown, and the recent investigations of Whitney, Dunstan, Moody, Friend, Cushman, Walker, and others. The electrochemical theory is now generally accepted. Consideration is given to the influences of physical and chemical heterogeneity, and of dissolved substances in the rusting process; also in the prevention of rust.

Saponification is discussed in its wider sense, meaning the resolution of oils and fats into glycerol and fatty acids, or their salts; the term is synonymous with "hydrolysis." After consideration of the general methods of saponification, the author takes up the Twitchell process, employing sulpho-aromatic compounds, but he does not feel justified in making detailed statements as to the mode of preparation of the "saponifier," owing to the secrecy imposed upon licencees using the process. A very good outline of the method of Connstein, Hoyer, and Wartenberg, using the fat-splitting enzyme, is included.

The very important topic of Sewage is condensed into about seven pages. Reference to the work of the Massachusetts Board of Health in connection with these problems, and tabulated data from the Reports of the Royal Commission (upon River Pollution?) are included in the article.

Artificial Silk is briefly treated in about four pages. The various processes of Chardonnet, Pauly, and others similar to them, and those employing cellulose thiocarbonate, are described; also some of the details of the apparatus employed. Various tests, and the properties of the several kinds of fiber, are included.

Smoke and Smoke Prevention fill only five pages, but the subject is considered chiefly from the point of view of the domestic open-grate fire—a mode of heating far more general in Great Britain than in this country. It is stated that manufacturers have demonstrated the possibility of smokeless coal combustion, through improvements in furnace construction, and by mechanical stoking, but no description is given of any of these devices. The chief remedies recommended for the smoke nuisance are the use of coke or anthracite or fuel gas.

Comparatively few of the more striking new developments in chemical industry happen to fall within the alphabetical limits of this volume, and some of the articles seem to give the impression that space limitations have hampered the writers more or less; yet the book as a whole maintains the standard of its predecessors; in its make-up and typography it is very satisfactory.

F. H. THORP

ACTION OF THE SALTS IN ALKALI WATER AND SEA WATER ON CEMENTS. By P. H. BATES, Chemist, A. J. PHILLIPS, Assistant Chemist, and RUDOLPH J. WIG, Associate Engineer Physicist, Bureau of Standards. Technologic Papers of the Bureau of Standards, Department of Commerce, No. 12 (November, 1912). Washington: Government Printing Office. pp. 157.

That concrete is subject under certain conditions to disintegration by sea water has been known for many years but just what these conditions might be has long baffled investigators. There are many instances where concrete structures have successfully withstood the action of sea water for many years and the closest inspection fails to reveal any signs of disintegration. This is true not only of concrete which is constantly submerged in sea water but also of concrete surfaces which are alternately submerged and exposed by the tides.

On the other hand, we have many instances where concrete has been seriously affected by the action of sea water, which action at times has caused complete disintegration. Laboratory tests on the action of artificial sea water on concretes seem to uniformly prove that concrete is subject to more or less rapid and complete disintegration and that this effect is apparently caused by the action of magnesium sulphate on the lime and alumina of the cement, there being formed hydrated magnesia and calcium sulpho-aluminate, both of which, because of their high content of water of crystallization, have a greater volume than the compounds which they replace.

The reclamation of the vast arid areas of our country by irrigation has called for the varied and extensive application of concrete. It was soon noticed that the concrete in many instances was being seriously affected, presumably by the alkali which was present in the soil in large percentage. The Agricultural Departments of the states of Colorado and Montana conducted extensive investigations along this line and accumulated much valuable data. As much of this irrigational work is being done under direct supervision of the Government, it was considered timely to inaugurate an extensive investigation. This was first conducted by the Structural Materials Laboratory at St. Louis and later undertaken by the Bureau of Standards.

This is the first report made on the results obtained both in the laboratory and under actual or field conditions, the latter being conducted at Atlantic City. In the laboratory experiments cement mortars and concretes of various compositions were exposed to the action of solutions of many alkaline salts and combinations of these salts and the chemical and physical effects observed. The conclusions drawn from these experiments may be briefly stated as follows: Cement mortars and concretes are disintegrated by the mechanical action of almost any salt in its pores if a sufficient amount of it is allowed to accumulate so that the crystals formed will exert an expansive action. This is not only true of concretes but porous stone, brick and other structural materials are disintegrated in the same manner. While in the laboratory mortars and concretes are disintegrated by the chemical action of various sulphate and chloride solutions, field tests show that such action is very slight and it is assumed that the concrete is protected by an impervious skin of calcium carbonate. Properly proportioned Portland cement concrete, when totally immersed, is apparently not decomposed by the chemical action of sea water. Natural slag and other cements tested in concretes showed normal increase in strength with age in sea water. There is no apparent relation between the chemical composition of a cement and the rapidity with which it reacts with sea water when brought into immediate contact. It is stated that tricalcium sulpho-aluminate could not be formed. While the sulphates are the most active constituents of sea water taken up by cement and the presence of chlorides accelerates their action, no definite sulphate compound could be established. Metal reinforcement is not subject to disintegration if embedded to a depth of 2 inches or over in well-made concrete. As this series of experiments extended over a period of only three and one-half years, these conclusions must be regarded more as observations than as definite conclusions. C. N. WILEY

ZINK UND CADMIUM UND IHRE GEWINNUNG AUS ERZEN UND NEBENPRODUKTEN. Von R. G. MAX LIEBIG, Hüttendirektor a. D. Mit 205 Figuren im Text und auf 10 Tafeln, sowie einem Titelbilde. Chemische Technologie in Einzeldarstellungen. Herausgeber: PROF. DR. FERD. FISCHER, Göttingen-Hamburg. Spezielle Chemische Technologie. Leipzig: Verlag von Otto Spamer. 1913. S. xvi + 598. Preis: geh., M. 30.00; geb., M. 32.00.

Until the appearance of the present volume, there existed only two treatises on the metallurgy of zinc, one by W. R. Ingalls (New York, 1903), and the other by Lodin (Paris, 1905). It has always been surprising that the Germans, who have books on most subjects, should not have issued a volume treating of zinc, especially when it is remembered that until 1906 Germany was the leading producer of this metal. The reason for this lies probably in the unfortunate custom of most zinc smelteries of not giving out information of prevailing practice. This prevents the zinc metallurgist from undertaking the task of preparing a treatise; and without considerable practical experience with the metal it is very difficult even for the well-versed metallurgist to sift the large amount of heterogeneous matter found in technical periodicals.

The author, retired from practical work, adds now to his acknowledged high rank as zinc metallurgist the merit of having written a masterly work upon the metal to which he had devoted his technical activity.

The subject is treated in ten chapters. At first are discussed the ores of zinc and cadmium, and the modes of purchasing and of sampling; then follows a brief review of the properties of zinc and its compounds. This introductory part closes with a description of work in the chemical laboratory, an appendix giving numerous chemical analyses of ores, intermediary and final products.

The extraction of zinc from its ores by smelting is treated historically under the usual five headings of English, Carinthian, Silesian, Belgian and Rhenish modes of operating; in an appendix are given other methods which do not fit into the general classification; the whole is introduced by a history of the metal. By the historical method of presentation the evolution of the different types of furnaces is brought out clearly. In Chapter V is taken up the calcining and roasting of ores; then follow the manufacture of clay vessels, the preparation of charges, the chemistry of reduction, the condensation of zinc vapor, details of the construction of some parts of the furnaces, ventilation of furnace room, removal of residues, and lastly, the refining of crude zinc. Chapter VI discusses briefly the metallurgy of cadmium, and Chapter VII the preparation of zinc white. The uses of zinc and its oxides and of cadmium receive some consideration. The different non-electric and electric smelting methods proposed are reviewed in Chapter IX. This is followed by a similar treatment of the numerous electrolytic processes which have been advocated, tested and mostly abandoned. A few statistical notes close the last chapter.

This general statement gives an idea of the ground covered; it is not desirable to go into details, nor is it necessary, as the whole has received a careful treatment from the chemical, mechanical, technical and economic points of view; everywhere we see theory and practice well combined.

As far as the contents are concerned, we have a great book. It seems a pity that everything is not perfect. There is, in the first place, no index. The author states that he did not provide any, as it would have had to be very long to be at all adequate; he has therefore elaborated the table of contents, making this do duty for an index. An index of this book would have taken up from 20 to 30 two-column pages. Considering that a book of 598 pages, $9^1/_4 \times 6^1/_2$ inches, is $2^3/_4$ inches thick, and has the cumbersome weight of five pounds, the hesitation of the author to increase the bulk finds an explanation. It is hoped that with the first reprint the publishers will use a thinner paper and thus reduce this thickness and weight of the book, and leave room for an index.

H. O. HOFMAN

INDUSTRIAL CHEMISTRY. A Manual for the Student and Manufacturer. Edited by ALLEN ROGERS, in Charge of Industrial Chemistry, Pratt Institute, Brooklyn, New York, and ALFRED B. AUBERT, formerly Professor of Chemistry, University of Maine, with Thirty-four Collaborators. 340 illustrations. New York: D. Van Nostrand Co. 1912. pp. xiv + 854. Price, $5.00.

To attempt to cover the field of Industrial Chemistry in a single volume is a heroic undertaking. The ideal method, without question, is to call upon specialists for the discussion of various topics, but the task is not lightened thereby. Because an author is competent to write upon a given subject, it does not follow that he is especially qualified for sorting out and pruning down the material to meet a specified space. It is, moreover, difficult to prepare material for the student who may be looking for a statement of general principles and at the same time meet the needs of the manufacturer who may desire specific details in his own particular line. In view of these facts, it may be fairly said that the volume in hand has been compiled with a degree of success which on the whole must be considered noteworthy. It must be remembered that the manufacturer in his own line will be reinforced with the special literature pertaining to his subjects, but the interrelation of chemical processes makes it desirable to have at hand a treatise which will give the descriptive matter of associated topics in sufficient detail for reference, even by the manufacturer.

Metallurgical subjects have been eliminated with one exception, that of the Manufacture of Iron and Steel. But having broken over the rule to this extent, the question may fairly be asked whether it would not have been equally justifiable to include a paper on alloys, bearing metals, etc. With the material on the Manufacture of Iron and Steel, it is commendable that a most excellent bibliography is given at the end of the paper. This feature is the more conspicuous for the reason that it is absent from many of the other discussions. In a book of this character, where the various topics must be treated in such a meager manner, it would seem that the greatest service could be rendered by listing the very best references obtainable. The list at the end of the topic on Iron and Steel is an excellent example of what one might wish to see at the end of other papers.

As an illustration of what seems to be a poor balance of treatment, considering the importance of the subjects, the fact is noted that the topic of Fuels is given 22 pages, 5 pages of which are taken up with a discussion of the manufacture of coal gas, water gas, and the regenerative furnace, topics which are treated more or less fully under other headings. Again, under the topic of Fuels, there are discussed such topics as Pyrometry, Calorimetry, and the Coking of Coal by both the bee-hive and the by-product ovens; so that the data on Fuels and the problems of combustion are meager. In contrast with this, it is noted that the topic of Producer Gas alone occupies 22 pages. The illustrative table of type fuels on page 76 is rather seriously in error. The analysis seems to have been taken from artificially air-dried samples. The coals of Illinois, for example, are shown as having 4 and 7 per cent. of moisture, and the factor for volatile combustible is 28.86 per cent., which would seem to represent a type of coal not found in that state. On page 72 the nitrogen factor for pine of 6 per cent. is, of course, a typographical error.

It might be a question whether more space might not have been given to the subject of Glycerine, 1 page, even though it might have been found necessary to cut down the topic of Laundering, 13 pages. Doubtless, the editors found it, in many instances, less embarrassing to cut down their own contributions than to control the size and scope of those of their collaborators. While it is easy to point out many instances where the material might have been presented differently, the work on the whole is admirably presented and is especially to be commended for its fresh and up-to-date treatment of processes as they are carried out in this country. The industrial wealth in many lines in our own country and the desirability of setting forth the development of processes which have resulted here instead of copying old-time and abandoned methods, even though classical in character, must be put down to the credit of this work.

S. W. Parr

Allen's Commercial Organic Analysis. Vol. VII. Fourth edition, entirely rewritten. Edited by W. A. Davis, B.Sc., A.C.G.I., and Samuel S. Sadtler, S.B. Philadelphia: P. Blakiston's Son & Co. 1913. pp. ix + 563. Price, $5.00.

Seventeen years have elapsed since the last edition of the volume under consideration appeared and the present revision is, to say the least, timely.

Volume VII deals with Vegetable Alkaloids (in this respect being a continuation of Volume VI), Glucosides, Non-Glucosidal Bitter Principles, Animal Bases, Ptomaines or Putrefactive Bases, Animal Acids, Lactic Acid and Cyanogen and Its Derivatives, in the order named. Each chapter has been written by a contributor especially qualified to treat the subject under consideration. The classification in some places seems to be somewhat incongruous, but this is explained by a statement in the preface by the editors that "In order to interfere as little as possible with the original plan of the work the old arrangement has been retained so far as this has been found practicable. In retaining the old classification the editors have specially considered those chemists who, having become habituated to the order in former editions, look to find information in the new work in much the same position as in the old one." In spite of this explanation, it would seem to have been better to have included the chapter on Vegetable Alkaloids in Volume VI. It is unusual and unnatural to discuss, in a work of eight volumes, alkaloids, lactic acid and cyanogen and its derivatives in the same volume.

In the main, the revision has been most painstaking and thorough and the subject matter has been brought well up to date. The subjects treated in the volume in hand form a class than which there is probably none more difficult from the standpoint of analysis and quantitative determination and therefore the editors and publishers are to be congratulated upon the completeness of the work. There are only a few instances where quantitative methods have been overlooked which should have been included, and these omissions are probably due to the fact that such methods are scattered most widely and frequently in the most obscure and difficultly accessible chemical and pharmaceutical literature. One notable example is the method given on page 155 for the determination of santonin in worm-seed or *Santonica.* The method given was published in 1899 and has undoubtedly proved very unsatisfactory in the hands of all those who have attempted to use it. In September, 1912, there was published by Fromme in the *Jahresbericht* of Caesar & Loretz of Hamburg a method for the determination of santonin in *Santonica* which is very satisfactory indeed.

It is unfortunate that the present volume cannot include the methods for the determination of alkaloids which will be contained in the forthcoming revision of the United States Pharmacopoeia and which will in most instances be different from those contained in the volume under review, but as the Pharmacopoeia will not appear for at least another year, it would perhaps be asking too much to delay the publication of the present volume until that time.

The paper, typography and binding of the book are excellent and it is to be highly recommended to all analytical and commercial chemists as a valuable working adjunct and practically a *vade mecum.*

CHARLES E. CASPARI

PHYSIKALISCHE CHEMIE DER HOMOGENEN UND HETEROGENEN GASREAKTIONEN, unter besonderer Berucksichtigung der Strahlungs- und Quantenlehre, sowie des Nernstschen Theorems. Von DR. KARL JELLINEK, Privatdozent an der Kgl. Technischen Hochschule Danzig. Mit 221 Abbildungen im Text und 104 Tabellen. Leipzig: Verlag von S. Hirzel. 1913. S. xiv + 844. Preis: geh., M. 30.00; geb., M. 32.50.

This extensive treatise doubtless began, as the title indicates, with a study of the statics and kinetics of gas reactions; but as the author became interested in the various recent developments of Physics and Chemistry these have been successively included. This gives to the table of contents the appearance of extraordinary heterogeneity. The first three chapters deal solely with the laws of thermodynamics, excepting in so far as the so-called Nernst "Theorem" is introduced. The fourth chapter develops the theory of radiation; Kirchoff's law, Maxwell's electromagnetic equations, pressure of radiation, the law of Stefan and Boltzmann, the law of Wien, and finally the Blanck radiation formula with a discussion of elementary oscillators. In this chapter the author follows very closely the treatment given by Planck in his "Vorlesungen über die Theorie der Wärmestrahlung." Continuing the discussion of the quantum theory, the fifth chapter deals with the specific heats of solids and the equations of Einstein, Nernst and Lindemann, the specific heats of gases, and the numerous chemical constants that have been related by various authors to the fundamental quantity h of the quantum theory.

Here ends the theoretical part, and next come chapters devoted to experiments on radiant heat and the proper oscillations within the molecule; the measurement of temperature and of thermal quantities; and at last a chapter upon equilibrium in gas reactions, where the author follows the methods of Haber's book, but without displaying Haber's unusual critical acumen. In fact, a number of very doubtful experimental results, obtained in some cases with the express intention of verifying a predetermined theory (for example, the hydrocyanic acid equilibrium, p. 664), the author accepts at their face value. The remaining chapters of the book deal with the kinetics of gas reactions and with the various chemical processes occasioned by ions, silent electric discharge and ions.

The book is written with intelligence but apparently without inspiration. In spite of enormous padding the volume is sufficiently well indexed to be convenient for reference. To a student interested in the quantum theory, as every chemist and physicist is bound to be ultimately, certain chapters offer a very complete bibliography and résumé of the scattered articles which have appeared during the past few years in this important field.

Gilbert N. Lewis

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NITRO-*o*-SULPHOBENZOIC ACID AND SOME OF ITS DERIVATIVES[1]

BY MARTIN BELL STUBBS

At the time the work upon which this article is based was carried out it was thought desirable to enlarge our knowledge of the substances closely related to *o*-sulphobenzoic acid, which had at that time only recently come into prominence because of its relation to benzoic sulphinide (or saccharin). The immediate object of the investigation was not accomplished and, as the work brought out but little of value, the results have been neglected and allowed to remain unpublished. Since then Taverne[2] has described a few of the compounds first brought to light in the course of this investigation. In some respects his results agree with those of the author. In some respects they do not, as will appear in the course of this article.

Preparation of the Nitro Acid.—One part of the anhydrous *o*-sulphobenzoic acid was weighed into a large beaker glass and two parts of fuming nitric and two parts of pure concentrated sulphuric acid poured over it and the beaker glass gently heated. As soon as the *o*-sulphobenzoic acid had dissolved in the mixed acids a reaction took place, as shown by considerable bubbling and the copious fumes of nitrogen oxides given off. The liquid was heated for some time until all the nitric acid had gone off, the beaker being shaken to facilitate this. After the nitric acid was off the liquid remained quiet, and traces of a crystalline substance began to appear on the sides of the beaker on shaking. The liquid was then cooled down and four or five times its volume of cold water added, when a small quantity of a white crystalline substance appeared, which was immediately filtered off and washed with cold water.

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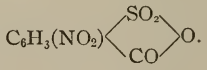
[1] Abstract of a dissertation presented in 1892 to the Board of University Studies of the Johns Hopkins University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Rec. trav. chim., **25**, 59 (1906).

When the hot concentrated sulphuric acid solution of the nitro acid is heated a little longer, after the crystalline product appears on the sides of the beaker, there is a sudden change of color from the pale yellow to a dark red, which rapidly becomes darker until a dark reddish brown or almost black, while gases are given off. This secondary action may be due to an action of the sulphuric acid on the nitro acid. It has not been investigated. However this may be, it was thought best not to allow this reaction to take place, as the red coloration produced was very hard to get rid of and the salts prepared from such an acid were less pure.

Anhydride of Nitro-o-sulphobenzoic Acid,



$C_6H_3(NO_2)\left\langle\begin{matrix}SO_2\\CO\end{matrix}\right\rangle O$.

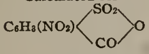
—This is the white crystalline substance which separated from the concentrated sulphuric acid solution on addition of cold water. It was dried between filter papers over sulphuric acid to prepare it for analysis. It was found to melt at about 212° (uncorrected).

In the analyses the carbon was determined by combustion in an open tube with lead chromate in a stream of oxygen. The sulphur was determined by Liebig's method and the nitrogen by Gunning's modification of Kjeldahl's method.

I. 0.34095 gram substance gave 0.35475 gram $BaSO_4$.
II. 0.2592 gram substance gave 0.26149 gram $BaSO_4$.
III. 0.6399 gram substance gave 0.03763 gram N.
IV. 0.46175 gram substance gave 0.02764 gram N.
V. 0.5403 gram substance gave 0.03478 gram N.

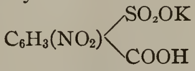
VI. 0.1570 gram substance gave 0.21021 gram CO_2 and 0.0340 gram H_2O.

VII. 0.1579 gram substance gave 0.2151 gram CO_2.

	Calculated for  $C_6H_3(NO_2)\left\langle\begin{matrix}SO_2\\CO\end{matrix}\right\rangle O$	Found						
		I	II	III	IV	V	VI	VII
S	13.97	14.30	13.86	....	....	....	...	...
N	6.11	...	...	5.86	5.98	6.43	...	...
C_7	36.67	...	...	....	....	....	36.51	37.13
H_3	1.31	...	...	....	....	....	2.14	...

The anhydride dissolves in cold water slowly, but easily in hot water or alcohol, forming the acid.

Taverne[1] nitrated the three sulphobenzoic acids by treating 1 gram of each of the anhydrous acids with 5 to 6 grams of nitric acid and, after solution had been effected, removing the nitric acid *in vacuo* over potassium hydroxide. In the case of the ortho acid a syrupy mass was obtained which, on standing *in vacuo* over sulphuric acid, began to crystallize and, at the end of two days, had been transformed into a porcelainlike mass which softened at about 90° and melted completely at 144°. He did not obtain the anhydride.

Acid Potassium Salt,  $C_6H_3(NO_2)\left\langle\begin{matrix}SO_2OK\\COOH\end{matrix}\right. + H_2O$.—The filtrate from the anhydride, consisting of the nitro acid and sulphuric acid, was diluted, and the sulphuric acid removed by means of calcium carbonate. The solution of the calcium salt thus obtained was then treated with potassium carbonate. The solution of the potassium salt was made strongly acid with hydrochloric acid and evaporated to crystallization. On cooling, the acid potassium salt separated out in fine yellow needles and tufts. These were separated from the mother liquor, boiled with animal charcoal and recrystallized, when the salt came out again as fine yellow needles, accompanied by a much smaller quantity of stout prisms and plates, apparently of the triclinic system and much resembling axinite. Some of the prisms were mechanically separated from the needles, dissolved in water and allowed slowly to crystallize over sulphuric acid, when a group of prisms was obtained. These were afterwards obtained in needles.

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[1] *Loc. cit.*

The purified salt, containing both kinds of crystals, was analyzed and found to contain one molecule of water of crystallization.

I. 0.18675 gram salt gave 0.0531 gram K_2SO_4.
II. 0.1500 gram salt gave 0.0430 gram K_2SO_4.
III. 0.15085 gram salt lost (at 140°) 0.0089 gram H_2O.
IV. 0.5456 gram salt lost (at 140°) 0.0327 gram H_2O.
V. 0.1989 gram salt gave 0.1477 gram $BaSO_4$.

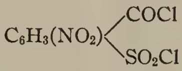
	Calculated for $C_6H_3(NO_2)\left\langle\begin{matrix}COOH\\SO_2K\end{matrix}\right. + H_2O$			Found		
		I	II	III	IV	V
K	12.87	12.76	12.84	....	....	...
H_2O	5.93	...	...	5.89	5.99	...
S	10.56	...	...	....	....	10.21

The analysis seems to show that the salt is pure, though, as the difference in crystallization would indicate, there may be an isomeric product present containing the same water of crystallization.

*Chlorides of Nitro-*o*-sulphobenzoic Acid.*—The acid potassium salt was dried, finely pulverized and mixed in an Erlenmeyer flask with a double quantity of phosphorus pentachloride. After the reaction had taken place the flask and contents were heated in a sulphuric acid bath to 120° until the oxychloride seemed to be off, then allowed to cool and washed repeatedly with large volumes of cold water until the washings were no longer turbid. The chloride was thus obtained as a light yellow oily-looking liquid, and was usually accompanied by a small amount of a white granular substance.

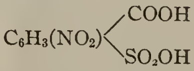
In two preparations of the chloride, when it was desirable to have it free from water, the wash water was poured off as much as possible and the chloride extracted from the remainder with ether. When the ether was distilled off the chloride remained behind as a reddish oil. The white granular substance was found to be insoluble in ether and was filtered off. It is insoluble in cold water, but dissolves on boiling, the solution giving a test for hydrochloric acid. When the solution is evaporated nearly to dryness small clusters of needlelike crystals of an acid are deposited. The small quantity of this substance obtained prevented any further investigation.

The nitro-*o*-sulphobenzoic dichloride was found to be insoluble in benzene and petroleum ether, but soluble in ordinary ether. It dissolves in boiling water with formation of the acid, and in cold alcohol with formation of the chloride ester, which is converted by water into the acid ester. With concentrated ammonia water or gaseous ammonia it reacts to form the sulphinide. Its constitution is shown by its reactions and mode of preparation to be.



$$C_6H_3(NO_2)\Big\langle\begin{matrix}COCl\\SO_2Cl\end{matrix}$$

An attempt was made to purify it by crystallization from ether at a low temperature, but without a satisfactory result. The chloride forms a viscous mass at —10°.



*Nitro-*o*-sulphobenzoic Acid*, $C_6H_3(NO_2)\Big\langle\begin{matrix}COOH\\SO_2OH\end{matrix} + xH_2O$.— The chloride was boiled with water until all had gone into solution, then boiled with animal charcoal, filtered and the filtrate evaporated to a syrup. Nothing crystallized out of this on standing exposed to the air. On standing over sulphuric acid for a long time small prisms crystallized out, but in insufficient quantity for an analysis. The very concentrated solution of the acid, when heated to a high temperature, turns dark and fumes with an odor like burnt sugar. The concentrated solution attacks organic matter, such as filter paper, very much as sulphuric acid or a concentrated solution of *o*-sulphobenzoic acid does. The anhydride also shows this property when heated to 90°. From the solution of the acid a series of salts was made.

Taverne[1] describes the free acid as being easily soluble in water and alcohol, very slightly in ether, insoluble in benzene, petroleum ether and chloroform. According to him it separates with 2 molecules of water and melts at 105° when dried in a desiccator.

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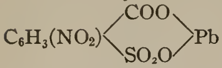
[1] *Loc. cit.*

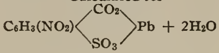
Lead Salt of Nitro-o-sulphobenzoic Acid,



$C_6H_3(NO_2)\genfrac{\langle}{\rangle}{0pt}{}{COO}{SO_2O}Pb + 2H_2O$.—This was prepared by boiling a solution of the acid with pure precipitated lead carbonate, filtering and evaporating the solution until a slight scum was formed on the sides of the vessel. The lead salt separated out in small acicular crystals containing two molecules of water of crystallization and easily soluble.

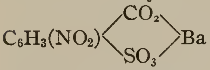
I. 0.2161 gram salt lost (at 160°) 0.0151 gram H_2O.

II. 0.1249 gram salt lost (at 160°) 0.0090 gram H_2O.

	Calculated for  $C_6H_3(NO_2)\genfrac{\langle}{\rangle}{0pt}{}{CO_2}{SO_3}Pb + 2H_2O$	Found	
		I	II
$2H_2O$	7.37	6.99	7.20

On evaporating the solution of the salt down to a small volume another lead salt separated out as a crust on the sides and bottom of the vessel. It was much more difficultly soluble than the crystallized salt and was apparently basic, as when dried at 100° and then heated to 140° it lost a little less than a molecule of water. No satisfactory analysis of this was obtained.

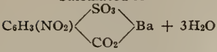
Barium Salt of Nitro-o-sulphobenzoic Acid,



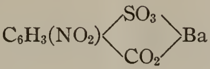
$C_6H_3(NO_2)\genfrac{\langle}{\rangle}{0pt}{}{CO_2}{SO_3}Ba + 3H_2O$.—This was prepared like the lead salt by boiling a dilute solution of the free acid with pure barium carbonate, filtering and evaporating the solution of the barium salt until a slight scum appeared. On standing several hours a moderate quantity of needlelike crystals appeared. These were recrystallized, dried and analyzed. They were found to contain three molecules of water of crystallization, all of which was lost by heating to 160°. The salt is not very easily soluble in water.

I. 0.2524 gram salt gave 0.1340 gram $BaSO_4$, and lost 0.0315 gram H_2O.

II. 0.3054 gram salt gave 0.15925 gram $BaSO_4$, and lost 0.0385 gram H_2O.

	Calculated fo  $C_6H_3(NO_2)\left\langle\begin{matrix}SO_3\\CO_2\end{matrix}\right\rangle Ba + 3H_2O$	Found	
		I	II
Ba	31.42	31.22	30.66
$3H_2O$	12.67	12.57	12.66

On evaporating the solution of this salt down to a small volume the salt separated out in small flakes over the bottom of the beaker. It was filtered off and dried between filter papers. On analysis it was found to be the anhydrous barium salt:

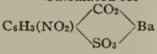


$$C_6H_3(NO_2)\left\langle\begin{matrix}SO_3\\CO_2\end{matrix}\right\rangle Ba$$

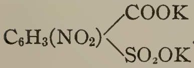
Taverne's[1] description of the barium salt obtained by him agrees with the above except that he says it is necessary to heat the salt to 200° to drive off all the water of crystallization.

I. 0.3058 gram salt gave 0.1854 gram $BaSO_4$.

II. 0.3602 gram salt gave 0.2208 gram $BaSO_4$.

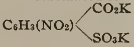
	Calculated for  $C_6H_3(NO_2)\left\langle\begin{matrix}CO_2\\SO_3\end{matrix}\right\rangle Ba$	Found	
		I	II
Ba	35.88	35.66	36.05

It was found to be much more difficultly soluble than the crystallized salt.

Neutral Potassium Salt of Nitro-o-sulphobenzoic Acid,  $C_6H_3(NO_2)\left\langle\begin{matrix}COOK\\SO_2OK\end{matrix}\right.$.—This was prepared by exactly neutralizing a solution of the acid salt with a dilute solution of potassium carbonate, filtering and evaporating until the salt separated. No crystals of this salt were obtained. The salt thus prepared contains no water of crystallization. It was dried at 100° and analyzed.

I. 0.3079 gram salt gave 0.1665 gram K_2SO_4.

II. 0.3627 gram salt gave 0.1951 gram K_2SO_4.

	Calculated for  $C_6H_3(NO_2)\left\langle\begin{matrix}CO_2K\\SO_3K\end{matrix}\right.$	Found	
		I	II
K_2	24.14	24.27	24.16

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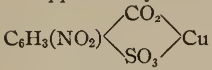
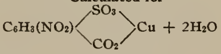
[1] *Loc. cit.*

Copper Salt of Nitro-o-sulphobenzoic Acid,



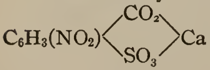
$C_6H_3(NO_2){<}\begin{matrix}CO_2\\SO_3\end{matrix}{>}Cu + 2H_2O$.—This was prepared by exactly precipitating the barium salt by a dilute solution of pure copper sulphate and filtering off the barium sulphate. The pale green solution of the copper salt so obtained was evaporated, first on an asbestos board and finally on a water bath kept at 70°. It was found that if the evaporation of the solution went on too rapidly a pale blue basic salt separated out which was difficultly soluble in water. The solution of the salt when brought down to a very concentrated solution deposited a fibrous crystalline mass of the copper salt. This was freed from the mother liquor as much as possible by the filter pump and then spread over an unglazed porcelain plate and kept over sulphuric acid for a couple of weeks, when the coating of salt became quite hard. It was scraped off, pulverized, and dried in an air bath at 70°, and again kept over sulphuric acid until the pale green powder began to whiten at the edges. It was then analyzed for water of crystallization. It was found to contain two molecules of water, like the lead salt, which it lost at 160°–170°.

I. 0.3463 gram salt lost 0.0363 gram H_2O.
II. 0.3543 gram salt lost 0.0375 gram H_2O.

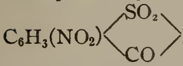
	Calculated for  $C_6H_3(NO_2){<}\begin{matrix}SO_3\\CO_2\end{matrix}{>}Cu + 2H_2O$	Found I	 II
$2H_2O$	10.46	10.48	10.58

The anhydrous salt is brown and when treated with water becomes green, but is difficultly soluble.

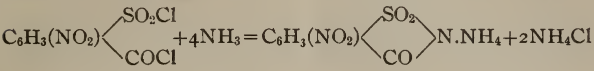
Calcium Salt of Nitro-o-sulphobenzoic Acid,



$C_6H_3(NO_2){<}\begin{matrix}CO_2\\SO_3\end{matrix}{>}Ca + xH_2O$.—This salt was prepared by boiling the free acid with pure precipitated calcium carbonate, filtering and evaporating to crystallization. It separates from a not too concentrated solution in fine short needles much resembling the barium salt.



Sulphinide of Nitro-o-sulphobenzoic Acid, $C_6H_3(NO_2)\Big\langle\begin{matrix}SO_2\\CO\end{matrix}\Big\rangle NH$.—This was prepared from the dichloride of the acid by treatment with dry ammonia. The reaction is represented thus:



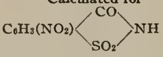
$$C_6H_3(NO_2)\Big\langle\begin{matrix}SO_2Cl\\COCl\end{matrix} + 4NH_3 = C_6H_3(NO_2)\Big\langle\begin{matrix}SO_2\\CO\end{matrix}\Big\rangle N.NH_4 + 2NH_4Cl$$

Two ways were tried to effect this reaction. The first was to pass dry ammonia gas over the chloride in a liquid or viscous state, stirring frequently to expose a fresh surface to the ammonia. After the experiment had proceeded as long as was deemed necessary the solid mixture of chloride and sulphinide was treated with water and the dissolved ammonium salts poured off from the unchanged chloride. Hydrochloric acid was then added to the solution, which was evaporated to a small volume, when part of the sulphinide separated out. This was recrystallized several times, but still contained considerable ammonium chloride, as the sulphinide is nearly as soluble as this salt. It is more soluble in alcohol than ammonium chloride, and this fact was also used for its purification.

A second method was found to give a much larger yield of the ammonium salt of the sulphinide. The dichloride was dissolved in ether and a rapid stream of ammonia passed into the solution. The ammonium salts were precipitated as a dirty yellow granular mass. This was filtered off and washed with ether. It consisted of the ammonium salt of the sulphinide with ammonium chloride, most of which was gotten rid of by repeated crystallization. The lead salt was made by boiling with lead oxide, filtering and evaporating to a small volume, when it separated on cooling. It was again dissolved and the lead exactly precipitated by dilute sulphuric acid, leaving the free sulphinide in solution. An attempt was made to crystallize it from water, but, as it is quite soluble, no great success was reached. It is less soluble in alcohol, and a small amount, about 0.250 gram, was obtained from a concentrated alcoholic solution. There was probably a little ammonium chloride still present, which would account for the high results in the determination of nitrogen.

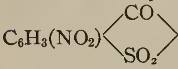
I. 0.2780 gram sulphinide gave 0.040216 gram N.

II. 0.2358 gram sulphinide gave 0.033016 gram N.

	Calculated for  $C_6H_3(NO_2)\left\langle\begin{matrix}CO\\SO_2\end{matrix}\right\rangle NH$	Found	
		I	II
N_2	12.28	14.45	13.53

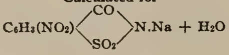
It was also attempted to prepare the sulphinide by passing dry ammonia gas into the anhydride suspended in ether, but without success.

Nitrobenzoic sulphinide is very soluble in water, less soluble in alcohol and insoluble in ether. It possesses an intensely bitter taste, greatly resembling quinine, but with a slightly sweet after-taste. It resembles in this respect *p*-nitrobenzoic sulphinide prepared by Noyes[1] from *p*-nitro-*o*-toluenesulphonamide, but differs from it in being more easily soluble.

Sodium Salt of the Nitrosulphinide,  $C_6H_3(NO_2)\left\langle\begin{matrix}CO\\SO_2\end{matrix}\right\rangle N.Na + H_2O$.—This was prepared by adding an excess of sodium hydroxide to a solution of the ammonium salt together with ammonium chloride and boiling off all the ammonia. It was then carefully neutralized with hydrochloric acid and evaporated to dryness, powdered and extracted with alcohol. After the alcohol had been distilled off the extract was dissolved in water and recrystallized several times until a small quantity of the needlelike crystals of the sodium salt was obtained. These contain one molecule of water of crystallization.

I. 0.2477 gram salt lost (at 150°) 0.0177 gram H_2O.

II. 0.1799 gram salt lost (at 150°) 0.0128 gram H_2O.

	Calculated for  $C_6H_3(NO_2)\left\langle\begin{matrix}CO\\SO_2\end{matrix}\right\rangle N.Na + H_2O$	Found	
		I	II
H_2O	7.08	7.18	7.11

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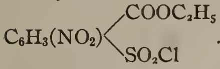
[1] This Journal, 8, 170.

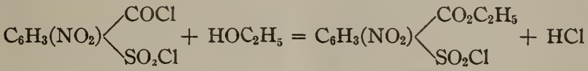
This salt is quite soluble in water, less so in alcohol. It has not the extremely bitter taste of the ammonium salt and the sulphinide, but is rather sweet with a slight bitterness.

Ethyl Ester Chloride of Nitro-o-sulphobenzoic Acid,



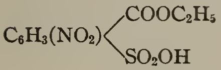
$C_6H_3(NO_2)\left\langle\begin{matrix}COOC_2H_5\\ SO_2Cl\end{matrix}\right.$

.—This was prepared by treating the chloride with cold strong alcohol and evaporating off the excess of alcohol. It forms an oily liquid. The reaction is represented thus:

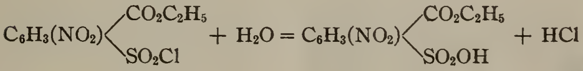


$$C_6H_3(NO_2)\left\langle\begin{matrix}COCl\\ SO_2Cl\end{matrix}\right. + HOC_2H_5 = C_6H_3(NO_2)\left\langle\begin{matrix}CO_2C_2H_5\\ SO_2Cl\end{matrix}\right. + HCl$$

When dissolved in hot water it formed the acid ethyl ester:



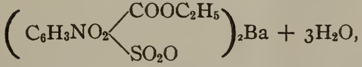
$$C_6H_3(NO_2)\left\langle\begin{matrix}COOC_2H_5\\ SO_2OH\end{matrix}\right.$$



$$C_6H_3(NO_2)\left\langle\begin{matrix}CO_2C_2H_5\\ SO_2Cl\end{matrix}\right. + H_2O = C_6H_3(NO_2)\left\langle\begin{matrix}CO_2C_2H_5\\ SO_2OH\end{matrix}\right. + HCl$$

From this was made, by neutralizing with barium carbonate,

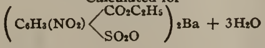
Barium Ethyl Nitro-o-sulphobenzoate,



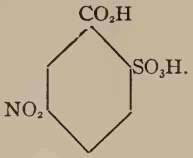
$$\left(C_6H_3NO_2\left\langle\begin{matrix}COOC_2H_5\\ SO_2O\end{matrix}\right.\right)_2Ba + 3H_2O,$$

crystallizing in colorless needles containing three molecules of water of crystallization.

I. 0.1397 gram salt lost (at 145°) 0.0100 gram H_2O.
II. 0.1663 gram salt lost (at 145°) 0.0121 gram H_2O.
III. 0.0208 gram salt gave 0.0071 gram $BaSO_4$.

	Calculated for  $\left(C_6H_3(NO_2)\left\langle\begin{matrix}CO_2C_2H_5\\ SO_2O\end{matrix}\right.\right)_2Ba + 3H_2O$	Found		
		I	II	III
$3H_2O$	7.30	7.16	7.27	...
Ba	18.54	....	....	19.87

An attempt was made to determine the position of the nitro group in the nitro acid by preparing the corresponding amino acid, diazotizing, and decomposing the diazo compound by boiling with water. This was not successful, though the results obtained made it appear probable that the nitro group is situated para to the sulpho group, and meta to the carboxyl. Taverne[1] has since shown that this view of the constitution of the acid is correct. He heated the anhydrous nitration product with phosphorus pentachloride up to about 180°, then boiled with water, when he obtained 2-chloro-5-nitrobenzoic acid, showing that the principal product of the nitration of *o*-sulphobenzoic acid is the nitro acid having the nitro group in the position represented in the formula



THE OXIDATION OF NITROGEN AND OXYGEN

By W. W. Strong

One of the most important problems in the chemistry of gas reactions is that of determining the exact mechanism of the reactions. What reactions are involved in the production of O_3; of NO?

Quite recently, R. J. Strutt[2] and his coworkers have published a series of papers on the reactions in which nitrogen is involved. Strutt's method consists in producing modifications of various substances in the electrical discharge and carrying these out of the region of the discharge ("afterglows") and then studying the chemical properties of the modified substances. During many of these reactions various characteristic spectra are emitted and it was hoped that the carriers of these spectra could be determined so that it would be possible to know the nature of the chemical reactions taking place in the various regions of arc and spark discharges through the nature of the light emitted.

[1] *Loc. cit.*

[2] P. Physic. Soc., **1910**, 66; **1911**, 147. P. Roy. Soc., **85A**, 219 (1911). Fowler and Strutt: *Ibid.*, **85**, 377 (1911); **86**, 56 (1911). See This Journal, **50**, 100.

Following are some characteristics of afterglows and different kinds of flames. The afterglows result from electrical discharge in vacuum tubes:

Pure oxygen	Weak afterglow
Air	Bright yellow; moisture has little effect
Pure nitrogen	None
Pure nitrogen	Glows when there is a spark discharge with capacity
Ozonized oxygen on H_2S or CS_2	Sky-blue flame possessing bands between $\lambda 2600$ and $\lambda 2300$
Ozonized oxygen on SO_2 or Sb or H_2, or CO or NH_3	No glow
Ozonized oxygen on acetylene	Swan spectrum
Ozonized oxygen on benzene	Weak glow
Ozonized oxygen on cyanogen	White glow
Nitrogen glow on mercury	Explosive compound
Nitrogen glow on acetylene	Cyanogen formed
Nitrogen glow on oxygen	Glow destroyed
Nitrogen glow on hydrogen	No effect
Nitrogen glow on nitric oxide	Greenish yellow flame giving the peroxide. The amount of this oxidation is taken as the measure of the amount of the glow

On account of the failure to liquefy the active modification of nitrogen, Strutt has assumed it to be a monatomic form of that element. It will therefore be designated by N.

The afterglow in air is considered as being probably due to the oxidation of nitric oxide by ozone, this being a kind of phosphorescent combustion. The nitrogen afterglow is not charged; is weakened by heating and intensified by cooling. The "yellowish green" flame characteristic of the high tension arc appears to be due to oxidation of oxides of nitrogen by ozone. This type of reaction may take place when:

(1) Ozone is mixed with NO or N_2O_2
(2) Ozone is mixed with NO_2 or N_2O_4
(3) N is mixed with NO or NO_2
(4) NO is fed into a Bunsen flame
(5) NO_2 is fed into a Bunsen flame

In the work of J. J. Thomson on positive rays the following kinds of ions have been detected:

$$\overset{-}{O_2};\quad \overset{-}{O};\quad \overset{+}{O};\quad \overset{+}{O_3};\quad \overset{+}{O_6};\quad \overset{++}{O}$$

$$\overset{++}{N};\quad \overset{+}{N};\quad \overset{+}{N_2};\quad \overset{+}{N_3};\quad \overset{+++}{N}$$

Assuming that dissociation takes place, we have O and N as well as O_2, N_2 and O_3, all these being neutral. If, then, the above are the only states of existence of oxygen and nitrogen matter, ozone and nitric oxide must be formed from one or more of the above products. The formation of ozone might take place in the following manner, *e* representing an electron:

$$\overset{-}{O_2} + \overset{-}{O} = O_3 - 2e \tag{1}$$

$$\overset{-}{O_2} + \overset{+}{O} = O_3 \tag{2}$$

$$\overset{-}{O_2} + \overset{++}{O} = O_3 + e \tag{3}$$

$$\overset{-}{O} + \overset{-}{O} + \overset{-}{O} = O_3 - 3e \tag{4}$$

$$\overset{-}{O} + \overset{-}{O} + \overset{+}{O} = O_3 - e \tag{5}$$

$$\overset{-}{O} + \overset{+}{O} + \overset{+}{O} = O_3 + e \tag{6}$$

$$\overset{-}{O} + \overset{++}{O} + \overset{++}{O} = O_3 + 3e \tag{7}$$

$$\overset{-}{O} + \overset{-}{O} + \overset{++}{O} = O_3 \tag{8}$$

$$\overset{-}{O} + \overset{+}{O} + \overset{++}{O} = O_3 + 2e \tag{9}$$

$$\overset{+}{O} + \overset{+}{O} + \overset{+}{O} = O_3 + 3e \tag{10}$$

$$\overset{+}{O_6} = 2O_3 - e \tag{11}$$

$$O + O + O = O_3 \tag{12}$$

$$\overset{+}{O} + \overset{-}{O} + O = O_3 \tag{13}$$

$$\overset{-}{O_2} + O = O_3 - e, \text{ etc.} \tag{14}$$

These are not all the possible equations representing what may take place. By assuming a certain distribution of each one of these "products," a certain distribution of velocities and of electrostatic charge, it would probably be possible to calculate the relative probabilities of each one of these reactions taking place. Naturally, other things being equal, the probability will be greatest for those equations containing positive and negative products. The most efficient method of producing ozone will be based upon the equation possessing the greatest probability of occurrence. At the present time we have no idea what the equation for the formation of ozone really is.

The electrical method promises to be of very great service in answering this problem, provided the reactions are carried on for comparatively large mean free paths.

The formation of nitric oxide can be an equally complex process.

(1) $\overset{-}{O_2} + \overset{++}{N} = NO + e + O$
(2) $\overset{-}{O_2} + \overset{+}{N} = NO + O$
(3) $\overset{-}{O_2} + \overset{+}{N_2} = 2NO$
(4) $\overset{-}{O_2} + \overset{+}{N_3} = 2NO + N$
(5) $\overset{-}{O_2} + \overset{+++}{N} = NO + 2e + O$
(6) $\overset{-}{O} + \overset{+}{N} = NO$
(7) $\overset{-}{O} + \overset{+}{N_2} = NO + N$
(8) $O + N = NO$
(9) $\overset{+}{O_3} + \overset{+}{N_3} = 3NO + 2e$
(10) $\overset{+}{O} + N = NO + e$, etc., etc.

It is seen that the formation of nitric oxide may be even more complex than the formation of ozone. Let us assume that the resultant product is formed by the combination of two "products" into a neutral molecule. The possible equations are then as follows:

(1) $\overset{-}{O_2} + \overset{+}{O} = O_3$
(2) $3O = O_3$
(3) $O + O_2 = O_3$
(4) $\overset{-}{O} + \overset{+}{O} + O = O_3$
(5) $\overset{-}{O} + \overset{-}{O} + \overset{++}{O} = O_3$

(1) $O + N = NO$
(2) $O_2 + N_2 = 2NO$
(3) $O + N_2 = NO + N$
(4) $O_2 + N = NO + O$
(5) $\overset{-}{O_2} + \overset{+}{N} = NO + O$
(6) $\overset{-}{O_2} + \overset{+}{N_2} = 2NO$
(7) $\overset{-}{O_2} + \overset{+}{N_3} = 2NO + N$
(8) $\overset{-}{O} + \overset{+}{N} = NO$
(9) $\overset{-}{O} + \overset{+}{N_2} = NO + N$
(10) $\overset{-}{O} + \overset{+}{N_3} = NO + N_2$

If the process is electrical, that is, if an intense state of ionization is necessary in order that the reaction take place, then only those reactions that are italicized would be possible. The relative intensity of the various "products" in the positive rays might be taken as indicating the relative probability of the occurrence of these reactions. Since rays of $\overset{-}{O}$ and $\overset{-}{O}_2$ are quite bright and since it is very unlikely that the products should collide simultaneously, we may conclude that ozone is formed by the following reaction:

$$\overset{-}{O}_2 + \overset{+}{O} = O_3$$

Since the concentration of dissociated products must be very small, the formation of nitric oxide probably takes place according to the following equations, the pressure and temperature being the main determining factors:

$$\overset{-}{O}_2 + \overset{+}{N} = NO + O$$

$$\overset{-}{O}_2 + \overset{+}{N}_2 = 2NO$$

$$\overset{-}{O} + \overset{+}{N}_2 = NO + N$$

At atmospheric pressure it is probable that the reaction is mainly:

$$\overset{-}{O}_2 + \overset{+}{N}_2 = 2NO$$

This conclusion is in agreement with Strutt's result that active nitrogen did not seem to be necessary for the production of nitric oxide.

It was thought that possibly the use of a corona discharge might indicate something concerning the nature of the reactions involved in the production of nitric oxide. Corona discharges may consist of streams of positive ions, of negative ions or of both positive and negative ions. A typical form of corona discharge is that between wires *F*, and cylinders *P*, as indicated in Fig. I. Either the active (wires where the electric field is very intense) or the passive electrodes (where the electric field is comparatively weak) may be grounded. By grounding the "active" electrode and passing a low voltage

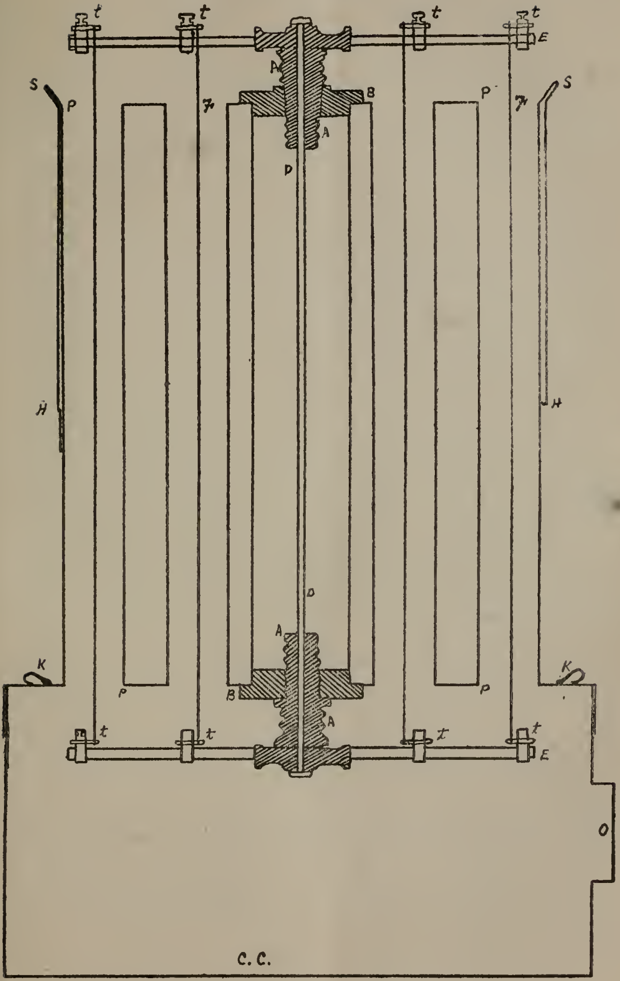


Fig. I

current through it, the temperature can be given any desired value. By using a suction fan, gases can be drawn through *F* and *O* through an absorbing solution of hydroxide. Sodium hydroxide (1.042 normal) was used in some of the experiments. By making the active electrodes porous the ions could be made either of oxygen or nitrogen. The particular electrodes of Fig. I consisted of No. 20 English gauge wire in 5-inch cylinders. The corona discharge could be made either positive or negative.

The corona discharge does not resemble any of the flames described above, so that it is at present impossible to get any clue as to what regions ozone and nitric oxide are being formed in. Following is a description of the positive and negative coronas. The alternating corona is a combination of both. The two photographs (Figs. II and III) were taken at the same voltage.[1]

In air the positive corona consists of fine branching, bluish purple brushes darting a cm. or more from the wire. When the ionic current density is great enough there is a thin, bluish purple film covering the wire. This is accompanied by a slight buzzing noise. The positive corona is not greatly affected by the presence of dirt. The brush discharge consists of straight stems of considerable luminosity, from which dart forth twiglike, purplish violet branches. The pitch of the hissing sound produced depends on the proximity of neighboring conductors.

Viewing a precipitation chamber with 30 or more wires axially placed within earthed cylinders gives a wavy, luminous effect somewhat like the northern lights effect. If the wire is not exactly concentric to the cylinder, the brush and branches swing to the region where the electric field is most intense. Looking at the cylinder end on gives one the impression that the whole region between the wire and the nearest side of the cylinder is filled with luminosity, though it is doubtful if this is the case. When this condition is reached and the voltage fluctuates slightly, occasional oscillatory sparks will take place. When a wire is more than 6 mm. in diameter only disruptive discharges occur.

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[1] For the electrical connections see P. Am. Inst. Elec. Eng., p. 1303, June, 1913.

In the case of a "dirty" wire several brushes will discharge per cm. length of wire, the intensity of the brushes constantly varying. Each brush starts from a bright point on the wire, the brightness of the point increasing with the size of the brush. Numerous points of less brightness also appear between the main brush points, the discharge from these points being too weak to give visible brushes.

The accompanying Fig. II is a photograph of the positive corona taken with the camera focused upon the end of the precipitation chamber represented in a later photograph. The lowest wire near the middle of the picture is the best focused and shows very clearly the stems and twiglike, purplish violet branches. The wire on the left side of the photograph is out of focus. Smoke and dust can easily pass through the purplish violet branch discharges. With the exception of the points at which these brush discharges originate, the wires show very little luminosity.

The negative corona consists of bright, stationary, reddish discharges from 3 to 5 mm. in length. No bright film is present. A loud buzzing noise is produced. The negative brush is but slightly influenced by the presence of surrounding conductors. Dirt decreases the noise and causes the discharge to become more localized and to start at a much lower voltage. On the wires of a precipitation chamber the negative corona fills only a comparatively small region of the cylinder and slight variation of the position of the wire from the axial position does not distort the radial symmetry of the discharge about the wire. The number of bright points on the wire is much larger than in the case of the positive corona. The relative intensities of the brushes do not vary greatly and their positions are fairly constant. When the sparking potential is reached the negative corona goes over into an arc very easily, much more easily, indeed, than is the case with the positive corona.

When the rectification of a corona is not complete, as is the case when various portions of the electromotive force wave are rectified, practically all combinations of a positive and negative corona discharge can be obtained. By using a small portion of the positive corona discharge it is possible to produce oscillatory sparks, these sparks being used to clean the electrodes of deposited material.

Inserting a spark gap and capacity in series with either a positive or a negative corona in the cylindrical precipitation chamber described above did not affect either kind of corona to any considerable extent, the observations being visual.

The accompanying Fig. III shows the negative corona, the camera being in the same position as that in which the positive corona was photographed. The electrical circuit was the same for both exposures, the direction of current only being changed. The outside cylinders were earthed. The actinic luminosity of the negative corona is very much less than that of the positive corona and is almost entirely confined to the region close to the active electrode. The number of bright points on the wire is seen to be much larger in the case of the negative corona. (The time of exposure of the negative and positive coronas was approximately the same.)

The results of the experiments are as follows:

(1) 1 cc. 1.042 NaOH solution neutralized in 12 minutes by a positive corona.

(2) 1 cc. 1.042 NaOH solution neutralized in 7.2 minutes by a negative corona.

(3) 1 cc. 1.042 NaOH solution neutralized in 13 minutes by a negative corona.

The energy consumption was about 300 watts and this would give about the same order of yield as is given by the Birkeland-Eyde, the Pauling and the Schönherr arc methods. Only a few runs were made as opportunity was afforded by the apparatus not being used for other purposes. It is hoped that a study of the ozone and nitric oxide yields under various conditions will furnish valuable information concerning the mechanism of these reactions, since we are able to partly control the ionic streams in these experiments.

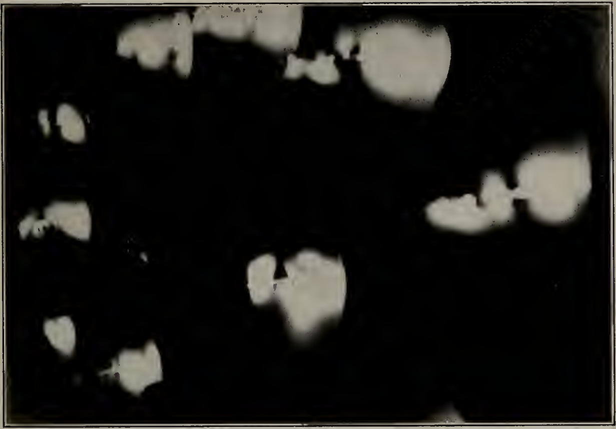

Fig. II

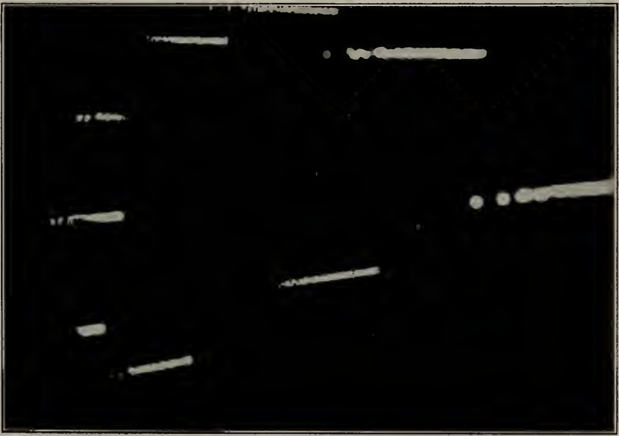

Fig. III

HIGH TENSION ELECTROLYSIS: A METHOD OF MEASURING HIGH VOLTAGE CURRENTS

By W. W. Strong

Among our most important laws connecting the phenomena of electricity and of matter are the laws of electrolysis. Indeed, it was through our knowledge of the conduction of electricity through electrolytes that the atomic nature of electricity was shown to be an actual fact. The relation between the amount of matter deposited at the electrodes and the quantity of charge which it has carried can be measured so accurately that the weight of this matter has been defined as being a measure of quantities of electricity.

Unfortunately one finds that very little quantitative work has been published concerning the phenomena of electrolysis when high voltages are used. One reason for this lack of data is due to the absence of sources of high and constant potential currents. It is well known that the potential given by an electrostatic machine is not constant (even though the circuit contain a comparatively large capacity) and the current available is almost infinitesimal in quantity. The so-called rectified currents possess electromotive force wave forms that are quite complicated and require much further study. Batteries such as small lead storage batteries are therefore practically the sole source of high tension potential currents and accurate experiments should be made to extend the ordinary laws of electrolysis to high voltage currents.

The arrangement of apparatus is indicated schematically in Fig. I.[1] A transformer, T, serves as a source of alternating voltage ranging between 5,000 and 60,000 volts. A graduated vessel, C', contains platinum electrodes E_1 and E_2 and a solution (about 0.1 normal sodium hydroxide in water was used) of electrolyte and is represented as being connected in series with the transformer and the corona wire A, the corona discharge being represented by C. When the potential reaches a certain value, a luminous glow appears on A and current flows between *A* and the grounded electrode *G E*. The cell *C′* may also be placed between *T* and the ground *G*. According to the above arrangement, the corona discharge from *A* is an

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[1] For a fuller description see an article on Electrical Precipitation, J. Frank. Inst., Sept., 1912.

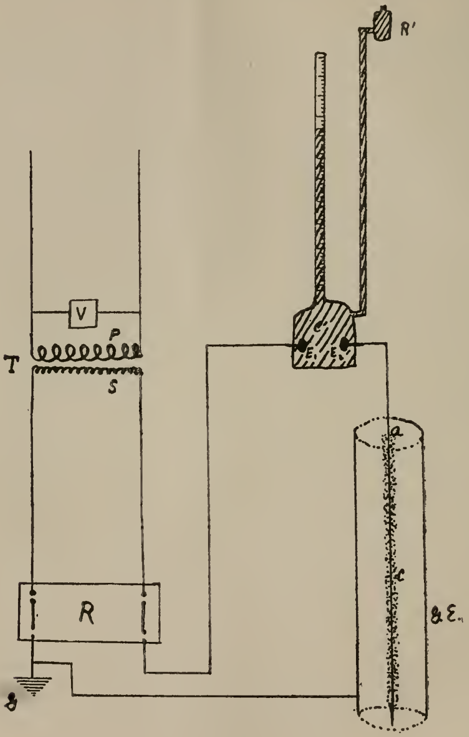

Fig. I

alternating positive and negative corona. By using a rectifier such as *R* the corona current from *A* may be made positive or negative at all times.

The direction of the current due to the corona will be represented by the direction of flow of the positive ions. When a unidirectional corona current is used the gas current is found to come almost entirely from the electrode in C′ that is positive. Hot gases can be passed through *C* and the amount of electrolysis measured for corona discharges in various kinds of gas. In the descriptive table the corona current due to a unidirectional corona depends upon the voltage and the portion of the wave form rectified.

(1) The gases are not given off at the electrodes according to the volume ratio ($2H_2 : O_2$). In many of the instances investigated practically all the gas moved in the same direction as the electric current.

(2) The total quantity of gas evolved was of the order of magnitude to be expected from Faraday's laws. In the present experiments[1] the form of the rectified current was not sufficiently well known to make possible the computation of the quantity of electricity carried.

(3) The currents used were the corona currents through a gas. The effective voltage varied between 10,000 and 35,000. When an alternating current was used, gas began to be liberated at a potential of about 17,000 volts effective. The flow of gas under these conditions was such as would make the positive corona current greater than the negative corona. This is in accord with the fact that for a given voltage the positive rectified corona current is greater than the negative rectified corona current.[2]

(4) The amount of electrolytic gas evolved appeared to depend upon the part of the circuit in which the cell was placed. Parts (16) and (17) of the table indicate this difference. On account of the sticking of the gas bubbles and the heating of the electrolytic solution (these solutions were boiled before being used) the experimental error was quite large. This error is probably not as great as that indicated in the following table.

(5) The electrolytic method promises to be of very considerable value in indicating the amount of rectification that exists in oscillatory and alternating currents and may be said

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[1] "The Positive and Negative Corona and Electrical Precipitation," P. Am. Inst. Elec. Eng., June, 1913.

[2] See paper on "The Positive and Negative Corona and Electrical Precipitation."

Corona Loss Experiments

	Gas evolved in cc. per min.	Sign of corona and voltage	Conditions of corona discharge	Remarks
(1)	0.029	Positive	Hot flue gas	Cell in series with rectifier and corona wire
(2)	0.031	Positive	Smoke	As above
(3)	0.037	Positive	Hot flue gas	As above
(4)	0.030	Positive	Hot flue gas	As above
(5)	0.0108	Alternating through rectifier gaps	Still room air	As above. Gas current is such as to make the active wire positive as above
(6)	0.0103	As above	Room air in motion	As above
(7)	0.026	Positive, 26,400 volts	Room air	As above. The gas current is nearly all in the direction of the current
(8)	0.0016	Positive, 36,000 volts	Negative electrode not grounded	As above
(9)	0.002	Alternating, no gaps, 38,000 volts	Still room air. One electrode free	As above. Gas current is such as to make the active wire positive

(10)	0.003	As above, 23,000 volts	Still air	As above. Gas current is such as to make the active wire positive
(11)	0.010	As above, 19,000 volts	Hot gases, 260°	As above. Almost all the gas current is such as to make the active wire positive
(12)	0.008	As above	Hot gases	Cell in series with the grounded wire. Gas current but slightly unidirectional
(13)	0.0232	Negative, 31,600 volts	Still room air	As above. Electrolysis was such as to indicate a negative corona
(14)	0.026	Negative, 31,600 volts	Hot air	As above
(15)	0.029	Positive, 22,500 volts	Hot air 260°	Cell in series with rectifier and corona wire
(16)	0.019	Positive	Still room air	As above
(17)	0.021	Positive	Still room air	Cell in series with the grounded electrode. Gas current in the direction of the electric current
(18)	0.027	Positive	Hot gases 260°	As above

to indicate changes in the medium in which the corona discharge is flowing. The corona current in (14) flows through hot gas, whereas in (13) it flows through room air. Apparently the corona current is the greater in the hot gas. When an alternating current is used, the corona is much more unidirectional in the hot gases, as is clearly shown in (9), (10) and (11).

(6) Placing the electrolytic cell on the grounded side of the corona discharge circuit seems to cause the electrolytic gas to be given off in the same way as for low voltage currents. This is indicated by (12).

EQUILIBRIUM IN THE SYSTEM: COBALT CHLORIDE AND PYRIDINE

By J. N. Pearce and T. E. Moore

Of the many possible systems containing as components pyridine, together with a single salt, only a comparatively small number have been studied in the light of the Phase Rule. The solubility method has been used for the investigation of systems containing the chloride,[1] bromide,[2] iodide[3] and nitrate[4] of silver, lead halides,[5] mercuric chloride[6] and lead nitrate.[7] Tombeck[8] used the vapor-pressure method in his study of compounds of copper salts with pyridine of crystallization. In an examination of some compounds of cobalt chloride with pyridine, Lang[9] believed that he obtained a product containing one molecule of Co_2Cl_4 to eight or ten molecules of pyridine. Reitzenstein[10] attempted to prepare compounds containing one, two and three to six molecules of pyridine to one molecule of cobalt chloride, but was unsuccessful. However, from cobalt chloride containing water of crystallization he made a compound which had the formula $CoCl_2.2C_5H_5N$. It had a bluish purple color and melted at 192°–195°. By using anhydrous cobalt chloride he was able to obtain the cherry-red compound $CoCl_2.4C_5H_5N$. No other reference to compounds of cobalt chloride and pyridine could be found in the literature.

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[1] Kahlenberg and Wittich: J. Phys. Chem., **13**, 421 (1909).

[2] Kahlenberg and McKelvey (not yet published).

[3] *Ibid.*

[4] Kahlenberg and Brewer: J. Phys. Chem., **12**, 283 (1908).

[5] Heise: *Ibid.*, **16**, 373 (1912).

[6] McBride: *Ibid.*, **14**, 189 (1910).

[7] Walton and Judd: J. Am. Chem. Soc., **33**, 1036 (1911).

[8] Tombeck: Ann. chim. phys., [7] **21**, 433 (1900).

[9] Lang: Ber. d. chem. Ges., **21**, 1578.

[10] Reitzenstein: Ann. Chem. (Liebig), **282**, 267.

The possibility of a relatively large number of solid compounds of cobalt chloride with pyridine of crystallization made it seem worth while to make a systematic study of this system. For this purpose solubility determinations were made at frequent intervals throughout the maximum possible range of temperature.

Materials

Cobalt Chloride.—Kahlbaum's best grade of cobalt chloride was recrystallized from absolute alcohol. A saturated alcoholic solution was first made at about 75° and then quickly cooled to 0°; the product of fine crystals was quickly filtered upon a Buchner funnel, sucked as dry as possible and placed in a vacuum desiccator over phosphorus pentoxide. To insure complete desiccation the drying was continued in an electrically heated glass tube, first in a current of dry hydrogen chloride gas for eight hours and, finally, in a current of dry hydrogen gas for three hours, the temperature in both cases being 175°. The anhydrous cobalt chloride thus prepared was preserved in tightly stoppered weighing bottles in a desiccator over phosphorus pentoxide. In order to test its purity the cobalt was determined electrolytically; the results of the analyses of four separate samples gave the following percentages of $CoCl_2$:

100.00, 99.97, 100.04 and 100.07. Mean 100.02.

Pyridine.—Kahlbaum's chemically pure pyridine, which had been standing over fused caustic potash for at least six months, was distilled, every possible care being taken to exclude moisture. Only that fraction passing over in the temperature interval between 115°–116° under 742–743 mm. was used in this work.

Potassium Permanganate.—Kahlbaum's chemically pure salt was dissolved in sufficient distilled water to make an approximately 0.05 N solution. In order to make sure that all of the oxidizable organic matter was destroyed, the solution was allowed to stand for two weeks. It was then standardized by means of pure oxalic acid according to the usual method.

Oxalic Acid.—The oxalic acid solutions used for standardization of the potassium permanganate solution and for precipitating the cobalt oxalate were prepared from very pure oxalic acid which had been purified according to the method of Morse.[1]

Ethyl Alcohol.—The large stock supply of 50 per cent. alcohol used in the precipitation of the cobalt chloride and for washing was made by the dilution of the ordinary 95 per cent. alcohol.

EXPERIMENTAL

The solubility determinations were made in an apparatus somewhat similar to that first used by Meyerhoffer and Saunders.[2] The apparatus consisted of a large Jena glass test tube fitted with a rotating stirrer consisting of a glass rod to which was attached a spiral of heavy platinum wire. To prevent the entrance of moisture the stirrer was provided with a mercury seal. The whole was then inserted in a constant temperature bath.

For all determinations between 0° and 34°.6 a large water thermostat was used. By means of submerged electric lights, a cooling coil, a contact toluene regulator and telegraph relay, any desired temperature could be obtained and kept constant to within a few hundredths of a degree. Constant temperatures between 34°.6 and 110° were secured by inserting the saturation tube through a tightly fitting cork into a larger boiling vessel containing a pure liquid having a boiling point approximately equal to the temperature desired. The boiling vessel was also provided with two small tubules, one for the insertion of a standard Anschütz thermometer into the vapor and the other for a long upright condenser.

The liquid in the outer vessel was kept at the boiling temperature by means of an electrically heated coil of fine platinum wire, electrical contact being made by means of mercury and the current regulated by a bank of incandescent lamps. By using this apparatus it was possible to obtain temperatures constant to within 0°.10 for a period of twenty-four hours or more, the temperature being always that of the vapor of the boiling liquid and subject only to the change due to variation in barometric pressure. To further aid in keeping the temperature constant throughout the boiling chamber, the vessel was entirely covered with asbestos paper. Ice and salt in different proportions, moistened with distilled water, gave temperatures between 0° and —20°. By carefully varying the proportions of solid carbon dioxide and ether, constant temperatures were obtained between —20° and —50°.3. These low temperatures quickly change, but it was found that by continually adding small quantities of solid carbon dioxide even these low temperatures could be kept constant during the time required for saturation. The temperatures below —20° were read on a pentane thermometer which permitted estimations with an accuracy of 0°.10, while ordinary standard Anschütz thermometers, graduated to tenths of a degree and permitting estimations as exact as one one-hundredth of a degree, were used for all temperatures above 0°.

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[1] Morse: Exercises in Quantitative Analysis, p. 116.

[2] Z physik. Chem., 28, 464 (1899).

Saturation of the solution at any temperature was secured by rapidly stirring a mixture of the solid and liquid phases, the stirrer being driven by an electric motor and making about five hundred revolutions per minute. Samples of the liquid phase were removed at intervals of one hour and analyses made to insure saturation. Saturation was found to be complete in one hour, although the time allowed for saturation was, in most cases, about four hours. After saturation the stirrer was stopped and the crystals allowed to settle for about twenty minutes. The liquid was then drawn out in quantities of from two to five cc. by means of a long glass tube, the end of which was covered with a fine cloth filter to prevent the entrance of crystals. This was quickly introduced into glass-stoppered weighing bottles, allowed to reach the room temperature and then weighed. When the temperature of the saturated solution was higher than that of the room the sampling tube was heated slightly above the temperature of the solution to prevent solidification within the tube.

Method of Analysis

A number of methods were available for the determination of the cobalt, but none of these could be safely used in the presence of pyridine. At first the electrolytic determination of cobalt was attempted, using the ammonium formate method of Smith.[1] This is both rapid and accurate for aqueous solutions of cobalt chloride, but the presence of pyridine prevented the complete precipitation of cobalt. This method was consequently abandoned and others applied. However, in each case, the pyridine interfered with the results. Finally, it was found necessary, in every case, to evaporate off the pyridine before making an analysis. The following method was finally decided upon as the most accurate and reliable under the existing conditions.

The weighed sample of the solution contained in the weighing bottles was placed in an air bath and kept at a temperature of about 120° until no odor of pyridine remained. It was then transferred to a beaker and dissolved in 50 per cent. ethyl alcohol. Oxalic acid was added in excess, precipitating the cobalt oxalate. This was allowed to stand at room temperature for about thirty minutes to insure complete precipitation. Under these conditions the filtrate gave no indications of cobalt with ammonium sulphide. It was filtered and the precipitate washed with the 50 per cent. alcohol until the filtrate gave no test for oxalic acid with calcium hydroxide. The filter containing the precipitate was placed in an air bath and heated at a temperature of 100° until all the alcohol had been evaporated. The cobalt oxalate was then dissolved on the filter by means of sulphuric acid (diluted 1 to 3). After washing the filter thoroughly, the solution of cobalt sulphate and oxalic acid was diluted to about 300 cc., heated almost to boiling, and titrated directly with standard potassium permanganate. Since the cobalt solution is generally pink in color, it is obvious that only dilute solutions can be used for titration. With these there is no difficulty in determining the end point with permanganate. Samples containing greater concentrations of cobalt chloride were treated as before, diluted to a definite volume, and aliquot portions of these taken for analysis.

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[1] Smith: Electro-Analysis, p. 135.

To show the accuracy of the method, the data obtained in the determination of the purity of cobalt chloride are given in Table I. The weights of the cobalt chloride given in the second column are made up to 250 cc. and 50 cc. portions of this solution taken for each analysis. The mean percentage of cobalt chloride found agrees very closely with that obtained by the electrolytic method in the absence of pyridine.

Table I

No.	$CoCl_2$ present in gram	$KMnO_4$ cc. 0.04758 N	$CoCl_2$ found in gram	Error in gram	Per cent. $CoCl_2$ found
1	0.1389	45.05	0.1391	0.0002	100.14
2	0.1411	45.72	0.1410	0.0001	99.92
3	0.1453	47.09	0.1455	0.0002	100.13
				Mean,	100.06

Mean of electrolytic determinations, 100.02

Solid Phases

The analysis of the solid phase was difficult in all cases. It was separated from the liquid by removing the stirrer from the tube and inserting a perforated platinum spoon by means of which crystals were lifted from the solution and allowed to drain within the tube at the exact temperature of equilibrium. The crystals thus obtained were freed from further adhering liquid by quickly pressing them between sheets of filter paper. They were then preserved in glass-stoppered bottles until analyzed. In order to ascertain their stability two samples of each solid phase were placed in desiccators, one over pyridine and the other in dry air. The difficulty in removing all the extraneous liquid from the crystals without the loss of pyridine from the compound itself gives results slightly high in pyridine, yet sufficiently accurate for determining the stoichiometric relations.

The freezing point of pure pyridine was found to be —48°.2 and that part of the curve between the latter temperature and —50°.3 is the freezing-point curve; *i. e.*, it represents the equilibrium between solid pyridine and the unsaturated solution. At —50°.3 the compound $CoCl_2.6C_5H_5N$ and solid pyridine separate out together, in contact with the liquid and vapor phases, and upon further cooling the entire mass solidifies. Since —50°.3 is the temperature at which the entire mixture freezes, there is no doubt that this temperature is very close to the true eutectic point. This point was found by placing the saturation tube in a Dewar flask containing solid carbon dioxide and ether and maintained at a temperature of about —65°. A thermometer and stirrer were inserted in the solubility tube and the mixture stirred slowly. The temperature gradually decreased until it was undercooled a few degrees, then it rose suddenly and remained at the temperature of —50°.3 until the mixture had entirely congealed, when the temperature again began to fall. This is a quadruple point, the invariant system consisting of four phases—solid pyridine, solid $CoCl_2.6C_5H_5N$, saturated solution and vapor.

The solubility remains practically the same with but slight increase from —50°.3 to +15°. The solid in equilibrium with the saturated solution between these temperatures has the composition $CoCl_2.6C_5H_5N$. These crystals are very minute and unstable, slowly giving up pyridine even in an atmosphere of pyridine. Owing to their rapid formation, the crystals were too fine to be identified even by means of a polarizing microscope. Their color is a bright pink bordering on the red.

The analysis of the crystals by two different methods, one for the pyridine content and the other for the cobalt chloride, agreed very closely. The crystals yielded 79.4 per cent. pyridine, while the calculated amount is 78.2 per cent. The high result is probably due to the pyridine adhering to the crystals.

From 15° to 70° the solubility gradually increases with rise in temperature. The solid phase now in equilibrium with the liquid has the composition $CoCl_2.4C_5H_5N$. These crystals are likewise very small, although somewhat larger than those of the previous compound. These also were too small to be accurately identified by the polarizing microscope. All that could be ascertained concerning their form is that they are not of the first system, and that they appeared to be hexagonal in shape. Their color is a very deep pink with a purplish cast. Upon analysis these crystals were found to contain 70.8 per cent. pyridine, whereas the theoretical value for the compound $CoCl_2.4C_5H_5N$ is 70.9 per cent. These crystals are quite stable in an atmosphere of pyridine, but when allowed to stand in dry air at ordinary temperatures gradually give up pyridine. At 15° we have another quadruple point at which there is equilibrium between the vapor, saturated solution, and the two solids $CoCl_2.6C_5H_5N$ and $CoCl_2.4C_5H_5N$.

Between 70° and 90° the solubility increases still more rapidly with the temperature. The solid now in equilibrium with the saturated solution has the composition $CoCl_2.2C_5H_5N$. It is composed of large monoclinic or triclinic crystals of the fifth or sixth order, having a purple color with a slightly bluish tint. Upon analysis they were found to contain 55.8 per cent. of pyridine, while the compound $CoCl_2.2C_5H_5N$ contains 55.0 per cent. At 70° we have a quadruple point, the four phases being vapor, saturated solution and the two solids $CoCl_2.4C_5H_5N$ and $CoCl_2.2C_5H_5N$.

From 90° to 110° the solubility increases very rapidly with relatively slight increase in temperature. The deep blue solid phase existing between these two points was found to be $CoCl_2$; it was found to be stable in pyridine-free air, but takes up pyridine rapidly when allowed to stand in an atmosphere of this solvent. The temperature 90° represents still another transition point at which vapor and the saturated solution are in equilibrium with the two solids $CoCl_2.2C_5H_5N$ and $CoCl_2$.

In order to test the relative stability of the four solid phases, *viz.*, $CoCl_2$, $CoCl_2.2C_5H_5N$, $CoCl_2.4C_5H_5N$ and $CoCl_2.6C_5H_5N$, samples of each were allowed to stand in a desiccator for three weeks over pyridine. Upon analysis all four gave results corresponding to the formula $CoCl_2.2C_5H_5N$, showing the latter to be the more stable at ordinary temperature.

The experimental results obtained are presented in Table II, which gives the number of grams of cobalt chloride per one hundred grams of solution and the number of grams of cobalt chloride soluble in one hundred grams of pyridine:

Table II

Composition of Liquid in Equilibrium with Solid $CoCl_2.6C_5H_5N$

Sample	Temp.	Time in hours	Weight sample	Weight $CoCl_2$ obtained	Gram $CoCl_2$ per 100 grams solution	Mean	Gram $CoCl_2$ per 100 grams pyridine	Mean
56	—50.3	1.2					0.42	
55	—45.0	1.2	2.2119	0.00926	0.4185	0.4185	0.4204	0.4204
52	—30.0	1.2	4.8486	0.02140	0.4194		0.4212	
53	—30.0	1.2	4.6014	0.01941	0.4217		0.4237	
54	—30.0	1.2	5.4849	0.02301	0.4204	0.4205	0.4222	0.4224
49	—19.6	1.4	4.8191	0.02031	0.4225		0.4243	
50	—19.6	1.4	6.1815	0.02466	0.3988		0.4007	
51	—19.6	1.4	7.0639	0.03114	0.4411	0.4208	0.4431	0.4227
46	—10.0	3.0	4.9500	0.02143	0.4330		0.4349	
47	—10.0	3.0	7.0530	0.03026	0.4290	0.4310	0.4309	0.4329
42	0.0	4.0	11.6558	0.05027	0.4307		0.4327	
43	0.0	4.0	4.8005	0.02062	0.4295		0.4314	
44	0.0	4.0	6.0773	0.02622	0.4313	0.4307	0.4338	0.4326
Transition Point *Composition of Liquid in Equilibrium with Solid $CoCl_2.4C_5H_5N$*								
38	23.0	4.0	4.6116	0.02653	0.575		0.578	
39	23.0	4.0	6.7697	0.03865	0.571		0.574	
40	23.0	4.0	6.3204	0.05555	0.563		0.566	
41	23.0	4.0	5.2493	0.02981	0.568	0.569	0.571	0.572

57	25.0	3.5	4.8210	0.02777	0.576		0.579	
58	25.0	3.5	4.7322	0.02723	0.575		0.578	
59	25.0	3.5	5.8328	0.03345	0.574	0.575	0.577	0.578
1	34.6	4.0	3.6465	0.02749	0.754		0.760	
2	34.6	4.0	4.3187	0.03179	0.736		0.741	
3	34.6	4.0	5.0137	0.03750	0.748		0.754	
4	34.6	4.0	5.3414	0.04053	0.759	0.749	0.765	0.755
36	37.6	4.0	7.0387	0.05402	0.767		0.772	
37	37.6	4.0	5.3951	0.04030	0.742	0.754	0.748	0.760
5	44.6	5.0	5.1533	0.04777	0.927		0.936	
6	44.6	5.0	5.4246	0.05170	0.953		0.962	
7	44.6	5.0	5.3447	0.05072	0.949		0.958	
8	44.6	5.0	5.4241	0.05261	0.970	0.950	0.979	0.959
9	47.2	4.0	5.0138	0.05113	1.020		1.030	
10	47.2	4.0	5.0706	0.05288	1.043		1.050	
11	47.2	4.0	5.2199	0.05206	0.997		1.007	
12	47.2	4.0	4.8233	0.04918	1.008	1.020	1.028	1.029
32	51.0	6.0	4.3211	0.04791	1.109		1.121	
33	51.0	6.0	3.9030	0.04339	1.113	1.110	1.124	1.122
13	55.0	4.0	4.9569	0.05898	1.190		1.204	
14	55.0	4.0	5.127	0.06027	1.188		1.202	
15	55.0	4.0	4.7318	0.05670	1.198	1.192	1.213	1.206

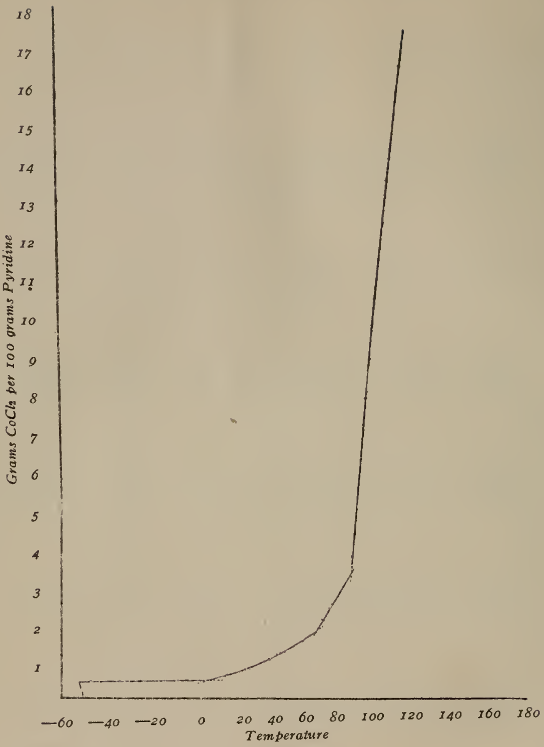
TABLE II—(*Continued*)

Sample	Temp.	Time in hours	Weight sample	Weight $CoCl_2$ obtained	Grams $CoCl_2$ per 100 grams solution	Mean	Grams $CoCl_2$ per 100 grams pyridine	Mean
16	60.0	4.0	5.3455	0.07080	1.324		1.342	
17	60.0	4.0	6.0555	0.08022	1.324	1.324	1.342	1.342
18	64.2	3.5	6.1928	0.09058	1.462		1.484	
19	64.2	3.5	2.9003	0.04232	1.459	1.460	1.482	1.483
60	68.0	3.0	4.7697	0.07555	1.584		1.609	
61	68.0	3.0	4.1115	0.06566	1.561	1.572	1.596	1.597
Transition Point								
Composition of the Liquid in Equilibrium with the Solid $CoCl_2.2C_5H_5N$								
34	74.8	3.0	2.7549	0.05634	2.045		2.087	
35	74.8	3.0	5.5110	0.11295	2.030	2.037	2.072	2.079
20	78.2	4.0	5.3976	0.12218	2.265		2.318	
21	78.2	4.0	5.9666	0.13645	2.288	2.276	2.342	2.330
62	79.8	4.0	3.2678	0.07955	2.431		2.492	
63	79.8	4.0	4.6397	0.11260	2.425	2.428	2.485	2.488
22	88.0	2.5	4.8881	0.16071	3.295		3.408	
23	88.0	2.5	3.2267	0.10550	3.272	3.284	3.387	3.397

Transition Point

Liquid in Equilibrium with Solid $CoCl_2$

24	96.5	5.0	3.8370	0.2775	7.234		7.796	
25	96.5	4.0	4.1234	0.2996	7.268	7.251	7.858	7.817
26	98.8	4.0	2.4947	0.1971	7.902		8.580	
27	98.8	4.0	2.4529	0.1955	7.970	7.936	8.661	8.862
28	106.0	3.0	1.0744	0.1321	(12.300)		(14.025)	
29	106.0	3.0	1.9391	0.2437	12.570		14.380	
30	106.0	3.0	1.4055	0.1765	12.570		14.380	
31	106.0	3.0	2.9736	0.3712	12.480	12.540	14.260	14.340
64	110.0	2.0	0.1012	0.01441	14.240		16.600	
65	110.0	2.0	0.2126	0.02993	14.090	14.165	16.398	16.500



Summary

The system cobalt chloride-pyridine has been studied for all temperatures between —50°.3 and 100°. The solubilities have been determined and the curve representing the equilibrium conditions established. It has been shown that cobalt chloride and pyridine form three distinct crystalline compounds. Reitzenstein had previously made the compounds $CoCl_2.2C_5H_5N$ and $CoCl_2.4C_5H_5N$, but the compound $CoCl_2.6C_5H_5N$ had not been isolated up to the present time. The compound $CoCl_2.2C_5H_5N$ was found to melt at from 195° to 200°, but we were unsuccessful in ascertaining the melting points of the other two, since they rapidly lose pyridine upon heating under atmospheric pressure.

The exact temperature limits within which these compounds can exist in equilibrium with a saturated solution have been determined. The compound $CoCl_2.6C_5H_5N$ exists as the solid phase between the temperatures $-50°.3$ and $+15°$, $CoCl_2.4C_5H_5N$ between 15° and 70°, $CoCl_2.2C_5H_5N$ between 70° and 90°, while between 90° and the boiling point of the saturated solution $CoCl_2$ is the stable, solid phase.

A new volumetric method for the determination of cobalt has been successfully applied.

Physical Chemical Laboratory
The State University of Iowa
July, 1913

REPORTS

THE SPECTROSCOPE IN ORGANIC CHEMISTRY[1]

Somewhat more than half a century ago, while engaged, with the assistance of Faraday, in preparing experiments for a Friday evening discourse in this Institution, Stokes observed that the spectrum of the electric light extended to five or six times the length of the visible spectrum when he employed prisms and lenses of quartz instead of glass. This extension occurs at the violet end of the spectrum, and consists of rays of high refrangibility to which the eye is insensitive, but which can be made apparent by means of a fluorescent screen.

At the time of this discovery, and in the years immediately following it, attention was being directed to the absorption of light by colored solutions, and to the possibility of identifying colored substances by the number and position of the dark bands in the spectrum of light transmitted through their solutions. Stokes saw that by his discovery of the extension of the spectrum beyond the visible region, this method of investigation might be applied to colorless as well as to colored substances. In a paper communicated to the Royal Society in 1862, he says: "The mode of absorption of light by colorless

[1] Address delivered before the Royal Institution of Great Britain, April 4, 1913.

solutions, as observed by the prism, affords, in many cases, most valuable characters of particular substances, which, strange to say, though so easily observed, have till very lately been almost wholly neglected by chemists." . . . "Having obtained the long spectrum above mentioned, I could not fail to be interested in the manner in which substances—especially pure, but otherwise imperfectly known organic substances—might behave as to their absorption of the rays of high refrangibility." He proceeded, therefore, to study the action of various organic solutions on the ultraviolet rays, and found that the mode of absorption generally was so constant and so characteristic that by this single property many substances could be identified. The substances which he examined included the best known vegetable alkaloids, all of which, with the exception of morphine and codeine, he was able to distinguish from one another by means of their absorption bands. This was a very remarkable anticipation of the results of later work on the subject, when we remember the great difficulties that must have been encountered in observing and measuring accurately the position of bands on a luminous screen.

While Stokes was engaged in these researches, Prof. William Allen Miller was simultaneously at work in the same field, and Stokes left the further development of the subject in his hands. Instead of a fluorescent screen, Miller employed a sensitive photographic plate for the reception of the spectrum. The rays of light were by this means made to register their own position and intensity, and a permanent record was obtained which could be studied at leisure. Miller failed, however, to "trace any special connection between the chemical complexity of a substance and its diactinic power." Struck by this fact, W. N. Hartley—now Sir Walter Hartley—commenced a systematic investigation of the whole subject, and it is to his researches, extending over a period of more than thirty years, that we owe, not only most of the knowledge which we now possess of the relation between the structure of organic substances and the action of such substances on the ultraviolet rays, but the elaboration of the convenient and elegant methods by which such investigations are now conducted.

The light derived from an ordinary source of illumination, such as an electric lamp, consists of waves of all degrees of refrangibility, and its spectrum shows a continuous band of color ranging from red to violet. The limits of this visible spectrum lie between the wave lengths 7600 and 3900.

If, instead of the electric light or other ordinary source of illumination, we employ the light emitted by one of the metals

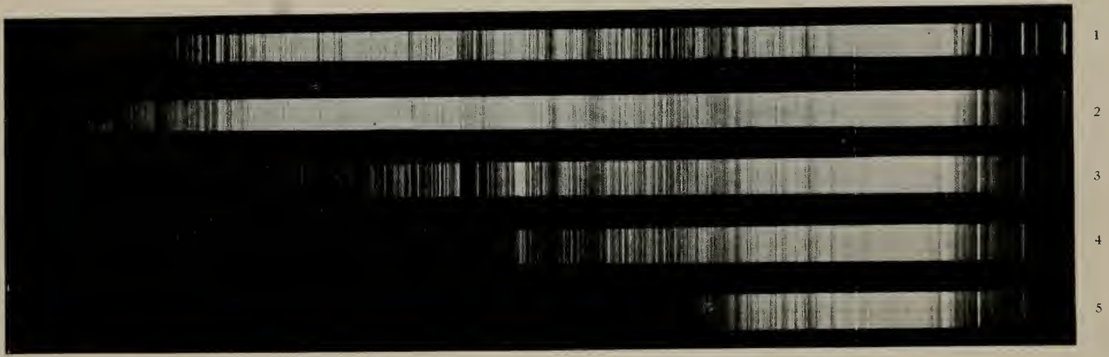


Fig. 1.—(1) Spark spectrum of nickel and iron; (2) the same after the light has passed through quartz, 10 mm. thick; (3) crown glass, 0.13 mm. thick; (4) crown glass, 0.33 mm. thick; (5) window glass, 1.62 mm. thick

when raised to a high temperature, the spectrum is seen to consist of a series of lines of different colors and intensities lying within the same limits as the visible spectrum. But there are rays beyond the red end of the spectrum and rays beyond the violet end which excite no sensation of luminosity in the eye. By allowing the spectrum to fall upon a screen which has been coated with a fluorescent substance, such as sulphate of quinine or a salt of uranium, these rays are rendered visible for a short distance beyond the violet. But it is only when we replace the glass apparatus, with which we have hitherto been working, by a quartz prism and lenses, and substitute a photographic plate for the eye, that the full extent of the spectrum beyond the violet is revealed (Fig. 1). This is the ultraviolet region—the region which Stokes opened up to investigation—and it is with the behavior of organic substances towards the rays of this part of the spectrum that we have mainly to do this evening.

When light is transmitted through a colored solution certain rays are absorbed, and dark bands corresponding to these rays appear in the spectrum. The importance of these bands as a means of distinguishing colored substances has long been recognized, and, as we have already seen, considerable progress had been made with their study fifty years ago. As the bands in this case are in the visible spectrum, no special means are required for their observation.

But when we extend this method of investigation to colorless substances, we are dealing with phenomena which lie hidden from the unaided eye, and our investigations are necessarily carried out with the help of photography.

The instrument employed in the study of absorption spectra consists of a spectroscope in which the eye-piece of the telescope is replaced by a camera. The photographic plate is set at such an angle as to bring all the rays emanating from the source of light into focus at its surface after they have passed through the resolving prism, and for this purpose it is necessary that the plate should have a very slight curvature. The prisms and lenses of the apparatus are made of quartz, which, unlike glass, is readily permeable by the ultraviolet rays. The source of light usually employed is that obtained by sparking one of the metals, such as iron, or a combination of metals, such as cadmium alloyed with lead and tin, selected so as to give a large number of lines spread as uniformly as possible over the whole ultraviolet region. The advantage of such a spectrum over a continuous spectrum is that the position of absorption bands, when they occur, can easily be determined with reference to the metallic lines whose wave lengths and place in the spectrum are known with great accuracy. In using the apparatus a photograph is first taken of the spectrum of the source of light. A layer of the substance to be examined, which, if a solid, must be dissolved in a suitable diactinic solvent, such as alcohol or water, is then interposed between the source of light and the slit of the collimator, and another photograph is taken. By comparison of the two photographs it is seen what effect, if any, the substance has had upon the transmission of the light.

When organic substances are examined in this way it is found that some allow light to pass freely through them. Others shorten the spectrum by absorbing the rays at the ultraviolet end to a greater or less extent, and are said to show general absorption. Others, again, possess the remarkable property of absorbing rays of a particular wave length, thereby producing gaps or bands in the spectrum; these are said to show selective absorption (Fig. 2).

In studying these phenomena in their relation to the chemical characters of a substance, it is of importance to determine not only the extent of the general absorption and the number and position of the absorption bands, but their degree of persistence, i. e., the range of concentration within which they are exhibited. It is necessary, therefore, to vary the concentration of the solution or the thickness of the layer so as to cover the whole phenomena of absorption. This is done by simply diluting the solution or diminishing the thickness of layer, on the one hand, until the entire spectrum is transmitted; and, on the other hand, by increasing the concentration or the thickness of the layer until no further characteristic absorptive effect is produced. Photographs (Fig. 3) are taken at each concentration, and a curve is drawn connecting the concentration and the absorption as measured with reference to the lines of the metal employed as a source of light. The values of the spectral lines are usually stated in wave lengths, but in these curves it is preferable to express them in reciprocals of wave lengths. It is also convenient to make use of the logarithms of the numbers representing the thicknesses of the layers examined, rather than the numbers themselves (Fig. 4).

If we now inquire whether the substances which affect light in one or other of the different ways already indicated have themselves anything in common, we find that it is with those which possess the structure characteristic of benzene and its derivatives that the power of absorbing the rays of particular parts of the spectrum is most frequently, although not exclusively, associated.

Organic compounds, or compounds containing the element

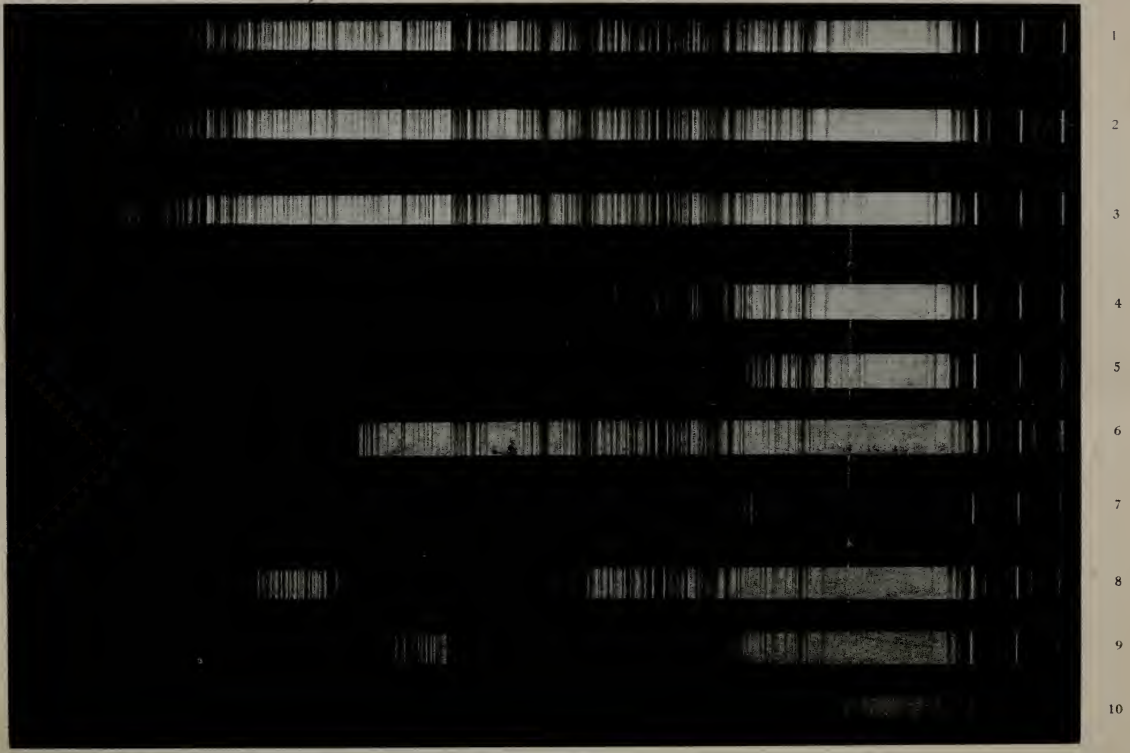


Fig. 2.—(1) Spark spectrum of nickel and iron; (2) and (3), the same after the light has passed through water and solution of cane sugar, respectively; alcoholic solutions of (4) pinene, (5) thiophene, (6) citric acid, (7) isatine, (8) phenol, (9) salicylic acid, (10) quinine hydrochloride; (4), (5) and (6) illustrate general absorption; (7), (8), (9) and (10) illustrate selective absorption

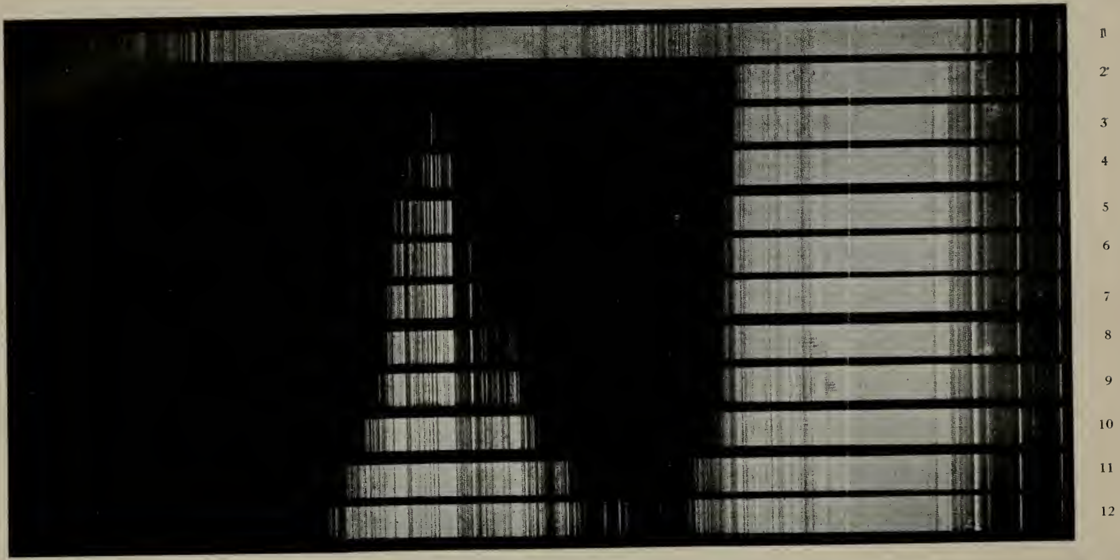


Fig. 3.—(1) Spark spectrum of nickel and iron; (2-12), the same after the light has passed through layers of 0.001 normal solution of salicylic acid from 90 to 4 mm. thick

carbon, are divided into fatty or aliphatic, in which the carbon atoms are united in an open chain, and cyclic, in which the carbon atoms form a closed chain or ring. Hexane, which is a constituent of liquid paraffin, may be taken as an example of the first class. This substance possesses six carbon atoms united together in a single chain and having attached to them fourteen hydrogen atoms, giving as the formula of the compound C_6H_{14}. This substance is highly diactinic or transparent to the ultraviolet rays, and nearly all compounds belonging to the same division of organic chemistry, such as alcohols, sugars and fatty acids, are either equally transparent to light, or only cut off a portion of the extreme ultraviolet rays of the spectrum.

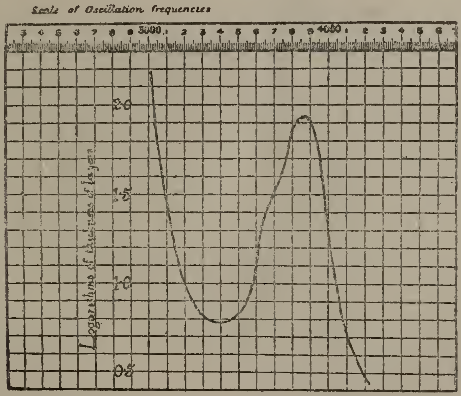


Fig. 4.—Salicylic Acid, 0.001 normal solution

If we now remove one atom of hydrogen from each of the two end carbon atoms of hexane, these atoms are in a condition to unite directly with each other, thus closing the chain. The substance so formed belongs to the cyclic division of organic compounds. It is known as cyclohexane, and has the formula C_6H_{12}, each carbon atom having two hydrogen atoms attached to it. This substance resembles hexane generally in its chemical properties, and behaves towards light in the same way; that is to say, it is practically diactinic or only cuts off some of the rays of light at the extreme ultraviolet end of the spectrum.

Speaking quite generally, it may be said that substances constituted like cyclohexane absorb more of the ultraviolet rather than those constituted like hexane.

But a wholly different condition is brought about if we suppose one atom of hydrogen removed from each of the six carbon atoms of cyclohexane. One linkage is thus set free in each of the six carbon atoms; and we obtain benzene. How these linkages are actually employed in benzene has never been determined with certainty. Sometimes they are represented as mutually neutralizing one another, sometimes as effecting a double link between the alternate pairs of carbon atoms. However this may be, the structure which bears the relation that I have indicated to the structure of hexane and cyclohexane is characteristic of the large group of organic substances of which benzene is the type. It is to this division of the cyclic compounds that the great majority of substances which show selective absorption, i. e., produce breaks or dark bands in the spectrum, belong. Here, then, we have a very important and a very general relation between the structure of organic substances and their absorption spectra.

The difference in the behavior of organic substances towards the ultraviolet rays, as exemplified in hexane and cyclohexane, on the one hand, and benzene on the other, is brought out very clearly when we examine some of their derivatives. If we replace an atom of hydrogen in hexane or cyclohexane by the monovalent group hydroxyl, we get substances belonging to the class of alcohols, and these substances are, like their parent substances, highly diactinic. If, on the other hand, we replace an atom of hydrogen in benzene by the same group we get carbolic acid or phenol, which, like benzene, exercises selective absorption on the ultraviolet rays, but gives a spectrum widely different from that of benzene.

Having dealt with the most general relation that has been observed between the structure of organic substances and their action on the ultraviolet rays, I propose to illustrate some of the more special relations by examples from the phenomena of isomerism. By replacing an atom of hydrogen in carbolic acid or phenol by the nitro group we obtain three distinct nitrophenols. The ultimate particles or molecules of these nitrophenols are all composed of the same elements, carbon, hydrogen, oxygen and nitrogen, and of the same number of atoms of each element. Such substances are said to be isomeric, i. e., they are made up of equal parts, although they do not possess the same properties. The difference between them lies in the arrangement of the parts relatively to each other; in this case in the position of the nitro group in relation to the hydroxyl group. On comparing the spectra of the three nitrophenols we find that they differ in quite a marked manner from one another, and afford an illustration of the important general rule that substances which have the same composition give different spectra if they differ in structure, i. e., in the arrangement of the atoms of their molecules.

It will have been noticed that the substitution of the nitro group for hydrogen in phenol has the effect of shifting the absorption band nearer to the visible region. One of the three nitrophenols has a yellow color, and in this case the gap in the spectrum cuts a little way into the violet end of the visible region. By the addition of soda to the solution the color is changed to red, and on examining the spectrum of this solution we see that the gap now extends far into the visible region. This example will serve to illustrate the close connection that exists between the study of absorption spectra and the origin of color, an interesting branch of the subject with which, however, it is impossible for me to deal within the limits of this discourse.

In the nitrophenols we have an example of what is known as structural isomerism, or position isomerism, because the phenomenon depends upon differences in the position or arrangement of the atoms within the molecule—in other words, on the internal structure of the molecule. But it is possible to have two substances of the same composition and structure not identical, but related to one another as an object is to its mirror image. Substances so related are termed optical isomers or stereoisomers. The spectra of isomers of this class, unlike those of structural isomers, do not differ. This leads to an important application of absorption spectra in chemical investigations. If two substances have the same composition but different spectra, we know that they must be structurally different; if, on the other hand, they have the same composition and the same spectra, and yet are not identical, there is a strong probability, although not a certainty, that they are optical isomers. To take an example: we know three substances of vegetable origin—papaverine (from opium), canadine (from the roots of *Hydrastis canadensis*), and tetrahydroberberine (a derivative of the principal alkaloid obtained from species of the barberry)—which have the same chemical composition represented by the formula $C_{20}H_{21}O_4N$. Papaverine and canadine differ widely in their spectra and in their structure; canadine and tetrahydroberberine have identical spectra, from which we should infer that they are in all probability stereoisomers, a conclusion which has been independently established by the most satisfactory chemical evidence.

In applying this reasoning in the investigation of substances of unknown structure, it has always to be borne in mind that while we may safely infer from dissimilarity of spectra dissimilarity of structure, we cannot always infer similarity of structure from similarity of spectra.

The study of absorption spectra has proved of special value in the investigation of substances capable of existing in two forms which may pass from the one into the other. It is rarely the case that both forms of such substances are stable, and it is often extremely difficult, or altogether impossible, on account of this instability to determine, by the ordinary chemical processes, which of the two possible forms the substance as we know it possesses. Such substances, however, frequently give rise to two series of stable isomeric methyl or ethyl derivatives, whose structure can be ascertained by chemical investigation. The parent substance, if not a mixture of the two forms, must correspond in structure with one or other of these derivatives, because it is a well-established fact that the introduction of the methyl or ethyl group into a substance in place of an atom of hydrogen does not appreciably alter the spectrum.

An example of this is afforded by the three substances isatine, methylisatine, and methylpseudoisatine. The structure of methylisatine and of methylpseudoisatine has been determined by chemical methods, but the structure of the parent substance isatine cannot be determined in this way. Is it constituted like methylisatine or like methylpseudoisatine? Inspection of the photographs of the spectra of the three substances shows that while there is a wide difference between the spectra of isatine and methylisatine, the spectra of isatine and methylpseudoisatine are almost identical, as we should expect them to be on the view that they are constructed alike.

This phenomenon, which is known as tautomerism, is due to the fact that some substances contain an atom of hydrogen or it may be a hydroxyl group, which readily shifts in position within the molecule, leaving its union with one atom to attach itself to another. Another example of this is afforded by cotarnine, a substance found in opium. The molecule of cotarnine possesses an atom of carbon which is directly combined with an atom of nitrogen, and has also united to it a hydroxyl group. Under the influence of certain reagents the hydroxyl group leaves the carbon atom and attaches itself to the nitrogen atom, but can readily, by an alteration of the conditions, be enticed back again to the carbon atom. The shifting of the position of the hydroxyl group is accompanied by other changes which, however, it is not necessary that we should take into account for our present purpose. In this case both of the tautomeric forms are, under certain conditions, stable. The form in which the hydroxyl is attached to the carbon is colorless, while the form in which it is attached to the nitrogen is yellow. The two forms have totally distinct absorption spectra. When one of the forms passes into the other under the influence of the appropriate reagent, the amount of change is proportional to the quantity of reagent added. It is possible, therefore, by taking photographs after the addition of each successive quantity of reagent to trace the progress of the change through all its phases, and to ascertain how much of each form is present at any time. This is done by comparison with a series of reference plates prepared by photographing mixtures in various definite proportions of two derivatives of cotarnine which possess the same spectra as the two parent forms.

Incidentally I may mention that these changes afford a basis for the measurement of the relative strength of alkalis and acids. For example, the change from the yellow to the colorless form of cotarnine takes place under the influence of alkalis, and by comparing the amount of change produced by equivalent quantities of different alkalis we obtain a measure of their strength.

The spectrographic method of investigation has been applied with marked success to the study of the vegetable alkaloids. Many of these substances, such as quinine, morphine, strychnine and atropine, possess powerful and valuable physiological properties, and their careful investigation is of the greatest importance to medical science. The number of atoms present in the molecule of an alkaloid is nearly always large, frequently as many as fifty or sixty. It is obvious, therefore, that the task of determining their exact relation to one another must be one of no little difficulty, and as a matter of fact the elucidation of the structure of an alkaloid is one of the hardest problems that the organic chemist can set himself. Any method, therefore, which assists the chemical examination is of peculiar value in this branch of organic chemistry.

In investigating an alkaloid or any organic compound, the first thing that the chemist has to do is to determine the elements of which it is composed, and the number of atoms of each of those elements present in one of its molecules or ultimate particles; in a word, what is known as its molecular formula. This is a comparatively easy operation: the difficulty comes when he attempts to determine the structure of the molecule, i. e., the exact manner in which the atoms are arranged with respect to one another. Now it may happen that two or more alkaloids have the same, or nearly the same, composition. The question arises, are they constructed on the same plan? It is in attempting to answer this question that the value of the spectroscope asserts itself. If on dissolving the alkaloids in some diactinic solvent and photographing their absorption spectra we find that the spectra are wholly different, we may conclude that in spite of the similarity, or even identity in their composition, the substances are not intimately connected with one another. If, on the other hand, we find that the spectra are the same, or very similar, it is probable that the substances are closely related. If the composition is the same and the spectra are the same, the substances are almost certainly optical isomers. Of substances related in this way we have already had an example in papaverine, canadine and tetrahydroberberine.

Among the rare alkaloids of opium are two, to which the names of laudanin and laudanosin, respectively, have been given. They have nearly, but not quite, the same composition, laudanosin containing one atom of carbon and two atoms of hydrogen more than laudanin; in other words, it is a homologue of laudanin. Substances so related hardly differ in their spectra, the replacement of one atom of hydrogen by the group of atoms CH_3 having very little disturbing influence, as we have already seen, upon the structure of a substance or upon its power of absorbing light. The spectra of laudanin and laudanosin being practically the same, it was inferred that they possessed the same structure and were probably homologous, before the fact had been ascertained by the usual chemical examination.

I must here advert again for a moment to Stokes' work on absorption spectra. I mentioned at the outset that he had been able to distinguish all the alkaloids he examined from one another by means of their absorption bands, except morphine and codeine. At that time the relation of these alkaloids to one another was unknown. We now know that they are homologues, and in that fact have the explanation of Stokes' failure to distinguish them by their absorption bands, and at the same time a striking testimony to the accuracy of his observations.

The examination of the spectra of laudanin and laudanosin not only revealed the fact that the two substances are homologues, but gave a clear indication as to the group of alkaloids to which they are most closely allied. When the spectra were compared with those of other alkaloids, they were found to resemble the spectra of corydaline and the related alkaloids so closely as to leave very little room for doubt that they are built on the same plan as these alkaloids. At the same time that

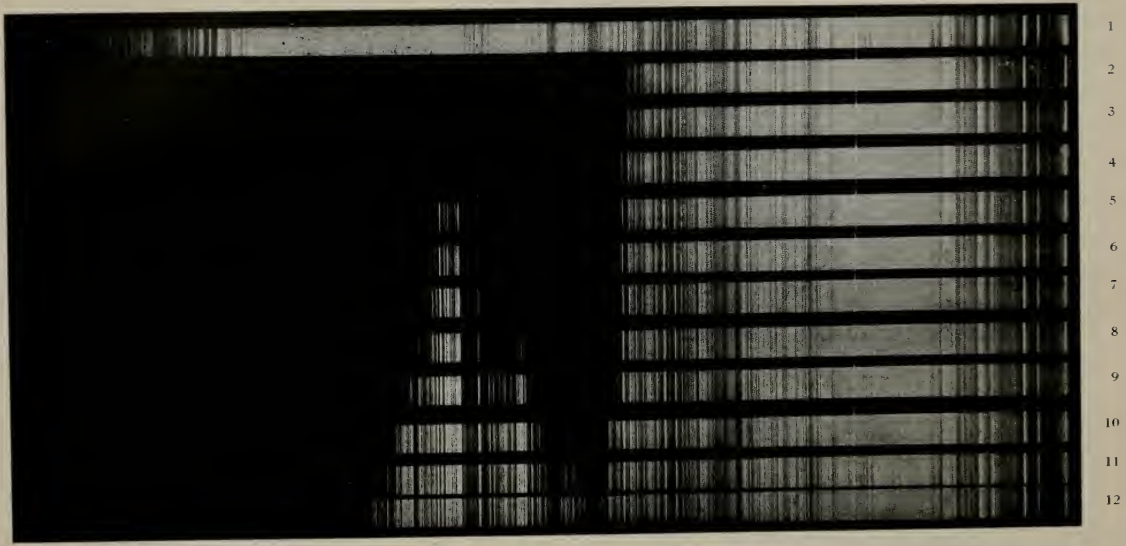


Fig. 5.—(1) Spectrum of nickel and iron; (2-12), the same after the light has passed through layers from 60 to 4 mm. thick of an alcoholic solution of morphine containing $^1/_{200}$ grain of the alkaloid

this conclusion was arrived at, practically nothing was known as to the chemical structure of laudanin and laudanosin, but the inference as to their close association with corydaline was subsequently fully justified by chemical investigation.

Apart from their structure there is another point of view from which the study of the spectra of the alkaloids is of interest and importance. These substances generally have very characteristic spectra by means of which they can be distinguished with certainty from one another, except when they are homologous or otherwise very closely related. The spectroscopic method may, therefore, be used with great advantage in examinations for the presence of alkaloids to confirm the results obtained by the usual chemical tests. The chemical tests are no doubt as a rule sufficiently distinctive, but considering the gravity under which they have frequently to be applied, it is unnecessary to insist on the value of the confirmatory evidence which can be obtained by the use of the spectroscope.

The minutest quantities of alkaloids can be detected by this means, the method rivalling the color reactions for the alkaloids in delicacy. Thus, with a quantity of strychnine not exceeding 0.002 of a grain, a clearly defined spectrum of the alkaloid can be obtained. The photograph of morphine already shown was obtained with 0.005 of a grain of the alkaloid (Fig. 5), and that of nicotine with 0.01.

The spectroscope serves not only for the detection, but for the estimation of alkaloids; by comparing the spectrum obtained with an unknown quantity of an alkaloid with a series of spectra obtained by photographing known quantities of the same alkaloid, it is possible to make quantitative determinations of a high degree of accuracy.

The use of the spectroscope in the detection and estimation of alkaloids in cases of poisoning possesses certain advantages of the highest importance. One is that the material is not destroyed. The solution which has been employed for the spectroscopic examination can be used afterwards for the chemical examination. Another is that a permanent record is obtained which is always available for reference.

So far my illustrations have been confined almost entirely to colorless substances, because it is in connection with the investigation of such substances that most of the recent advances in the subject have been made.

As my last example, I shall take the case of a colored substance in which the method has been applied within the last year with marked success.

It will be remembered that considerable uneasiness was caused when it became known sometime ago that nitrogen peroxide is sometimes employed to bleach flour. In the course of an inquiry into the subject, it became necessary to determine the nature of the coloring matter naturally present in flour. It was known that many of the yellow and orange pigments, so widely distributed throughout the vegetable kingdom, are either closely connected or identical with carrotene, the orange coloring matter of carrots, and it had been suggested that the coloring matter of unbleached flour might be identical with, or belong to the same class of coloring matters as this substance. It was impossible, however, to prove this by the usual chemical methods, because the amount of coloring matter in flour is so minute that its isolation in a pure state, and in sufficient quantity for chemical analysis, was hardly practicable. Carrotene, however, can be prepared in a pure state, and the happy idea occurred to Dr. Monier Williams, of the Local Government Board, who was conducting the investigation, to photograph its absorption spectrum and compare it with that of the coloring matter of flour, which could easily be obtained in the minute quantity required for this purpose. Inspection of the photographs shows that the spectra are very similar. There cannot, therefore, be any doubt that the coloring matter of flour, if not identical with, is closely allied to carrotene.

The underlying causes of the relations between chemical structure and absorption spectra have been the subject of much speculation. Hartley considers that the phenomena of absorption are intimately connected with the vibration of the atoms within the molecule. This view has much to recommend it, but obviously its application is limited by the present imperfect state of our knowledge of the internal mechanism of the molecule. A theory has been advanced according to which absorption bands are only exhibited by compounds whose molecules are in a state of change or flux. In the case of benzene, for example, the old idea is revived that the carbon atoms are linked together by alternate double and single bonds, which are perpetually changing positions. The presence of the bands in the spectrum of benzene is supposed to be in some way connected with these changes. Substances, however, are known which have banded spectra in regard to which such an explanation is inadmissible.

Quite recently a promising attempt has been made to bring the production of banded spectra into relation with the theory of electrons.

It must be confessed, however, that no satisfactory explanation of the phenomena of absorption has yet been formulated, and that the theoretical development of the subject lags behind its practical application. JAMES J. DOBBIE

SOME FURTHER APPLICATIONS OF THE METHOD OF POSITIVE RAYS[1]

The method to which I shall refer this evening is the one I described in a lecture I gave here two years ago. The nature of the method may be understood from the diagram given in Fig. 1. A is a vessel containing the gases at a very low pressure; an electric discharge is sent through these gases, passing from the anode to the cathode C. The positive electrified particles move with great velocity towards the cathode; some of them pass through a small hole in the center, and emerge on the other side as a fine pencil of positively electrified particles. This pencil is acted on by electric forces when it passes between the plates L and M, which are connected with the terminals of a battery of storage cells, and by a magnetic force when it passes between P and Q, which are the poles of an electromagnet. In the pencil before it passed under the influence of these forces there might be many kinds of atoms or molecules, some heavy, others light, some moving quickly, others comparatively slowly, but these would all be mixed up together. When they are acted on by the electric and magnetic forces, however, they get sorted out, and instead of traveling along the same path they branch off into different directions. No two particles will travel along the same path unless

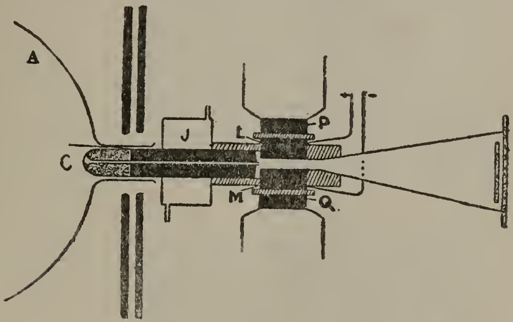


Fig. 1

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[1] Address delivered before the Royal Institution of Great Britain, January 17, 1913.

they have the same mass as well as the same velocity; so that if we know the path of the particle we can determine both its mass and its velocity. In chemical analyses we are concerned more with the mass than with the velocity, and we naturally ask what is the connection between the paths of particles which have the same mass but which move with different velocities. The answer is that all such paths lie on the surface of a cone, and that each kind of particle has its own cone; there is one cone for hydrogen, another for oxygen, and so on. Thus one cone is sacred to hydrogen, and if it exists there must be hydrogen in the vessel; so that if we can detect the different cones produced from the original pencil, we know at once the gases that are in the tube. Now, there are several ways of identifying these cones, but I shall only refer to the one I have used in the experiments I wish to bring before you this evening. These moving electrified particles, when they strike against a photographic plate, make an impression on the plate, and a record of the place where they struck the plate can be obtained. Thus, when a plate is placed in the way of the particles streaming along these cones, the sections of these cones by the plate (parabolas) are recorded on the photograph, hence we can identify these cones by the parabolic curves recorded on the photograph, and these parabolas will tell us what gases are in the vessel.

The first application of the method which I shall bring before you this evening is to detect the rare gases in the atmosphere. Sir James Dewar kindly supplied me with two samples of gases obtained from the residues of liquid air; the samples had been treated so that one might be expected to contain the heavier gases, the other the lighter ones. I will take the heavier gases first. The photograph for these is shown in Fig. 2. When the plate is measured up it shows a faint line corresponding to the atomic weight 128 (xenon), a very strong line corresponding to the atomic weight 82 (krypton), a strong argon line 40 (argon), and the neon line 20. There are no lines unaccounted for, and hence we may conclude that in the atmosphere there are no unknown gases of large atomic weight occurring in quantities comparable with those of xenon or krypton. This result gives an example of the convenience of the method, for a single photograph of the positive rays reveals at a glance the gases in the tube. I now turn to the photograph of the lighter constituents shown in Fig. 3; here we find the lines of helium, of neon (very strong), of argon, and in addition there is a line corresponding to an atomic weight 22, which cannot be identified with the line due to any known gas. I thought at first that this line, since its atomic weight is one-

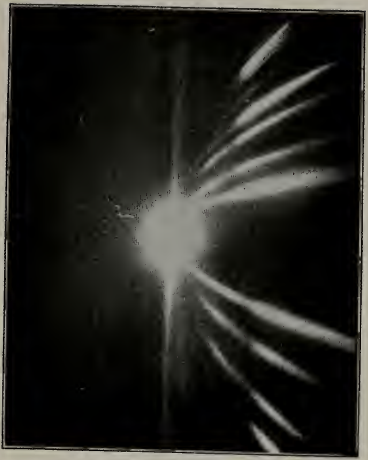

Fig. 2

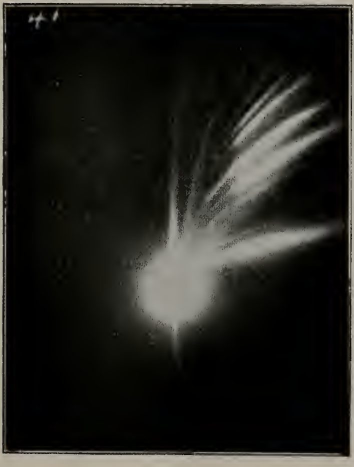

Fig. 3

half that of CO_2, must be due to a carbonic acid molecule with a double charge of electricity, and on some of the plates a faint line at 44 could be detected. On passing the gas slowly through tubes immersed in liquid air the line at 44 completely disappeared, while the brightness of the one at 22 was not affected.

The origin of this line presents many points of interest; there are no known gaseous compounds of any of the recognized elements which have this molecular weight. Again, if we accept Mendeléeff's Periodic Law, there is no room for a new element with this atomic weight. The fact that this line is bright in the sample when the neon line is extraordinarily bright, and invisible in the other when the neon is comparatively feeble, suggests that it may possibly be a compound of neon and hydrogen, NeH_2, though no direct evidence of the combination of these inert gases has hitherto been found. I have two photographs of the discharge through helium in which there is a strong line, 6, which could be explained by the compound HeH_2, but, as I have never again been able to get these lines, I do not wish to lay much stress on this point. There is, however, the possibility that we may be interpreting Mendeléeff's law too rigidly, and that in the neighborhood of the atomic weight of neon there may be a group of two or more elements with similar properties, just as in another part of the table we have the group iron, nickel and cobalt. From the relative intensities of the 22 line and the neon line we may conclude that the quantity of the gas giving the 22 line is only a small fraction of the quantity of neon.

Let me direct your attention again to the photograph of the heavier gases in the atmosphere. You will notice that the parabolas corresponding to many of the elements start from points which are all in the same vertical line; this indicates that the atoms or molecules which form these parabolas all carry the same charge. Several of these lines, however, do not follow this rule; you will notice, for example, that the neon line has a prolongation which comes nearer than the normal line to the vertical line drawn through the undeflected spot. Measurement of the photograph shows that the neon line begins at a distance from this vertical line which is only half the normal distance; this shows that some of the neon atoms in the positive rings possess two charges of electricity; the majority of them, however, possess only one. If you examine the argon line you will find that it comes even nearer to the vertical than the neon line; in fact, it begins at a distance from the vertical only one-third of the normal distance; this proves that the argon atom can have as many as three charges of electricity. If now you examine the krypton line you will find that it comes nearer to the vertical line than even the argon; its least distance is one-fourth of the normal distance, showing that the krypton atom may have as many as four charges. The mercury line comes so close to the vertical line that it is only on large photographs that it can be seen that there is in reality an interval; this interval is only one-eighth of the normal interval, showing that mercury may acquire eight positive charges, i. e., that it may lose eight corpuscles. The mercury atom when it is on this line must have only the normal charge, i. e., it must have regained all but one of the corpuscles it previously lost; if it had retained two positive charges it would have been on the line corresponding to the atomic weight 200/2 or 100; if it had retained 3, or 4, 5, 6, 7, 8, on the lines corresponding to the atomic weights, 200/3, 200/4, 200/5, 200/6, 200/7, 200/8, respectively. All these except the last have been detected on the plate. The lines corresponding to the multiple charges on krypton, argon and neon have also been detected. It appears, then, that in a vacuum tube a mercury atom, for example, may be ionized in two ways; in the one way the atom loses one corpuscle, in the other it loses eight. I would suggest that these two types of ionization may result from the two different types of collision which the atom must experience. The first type is collision with a corpuscle; since the corpuscle is an exceedingly small body moving with a very great velocity, it can pass freely through the atom, and the collision it makes with the atom is really a collision with a corpuscle inside the atom; this may result in the corpuscle it strikes acquiring such a great velocity that it is able to escape from the atom; this type of collision will result in the detachment of a single corpuscle. The second type of collision is when the atom collides with another atom and not with another corpuscle; the result of this collision may be that the atom suffers a sudden change in its velocity. This change is not at first shared by the corpuscles, so that these just after the collision may have a very considerable velocity relative to the atom. If there are several corpuscles which are comparatively loosely attached to the atom, these may all be detached from it and leave it with a positive charge corresponding to the number shaken out. It is this type of collision which we regard as giving the multiply-charged ions, and we see that the magnitude of the charge is a measure of the number of corpuscles in an atom which are readily detachable from it. We have seen that the greater the atomic weight the greater the charge it can acquire, the maximum charge being roughly proportioned to the square root of the atomic weight, hence the heavy elements have a larger number of detachable corpuscles than the lighter ones.

Another application of the method I should like to bring before you is the use of it for the discovery and investigation of a new substance. I have in previous lectures said that sometimes there appeared on the plates a line corresponding to a particle with an atomic weight 3; this must either be a new element or a polymeric modification of hydrogen, represented by H_3. The other possibility that it is a carbon atom with four charges is put out of court by the fact that it frequently occurs when the carbon line is exceedingly faint, and when there is not a trace of a carbon atom with even two charges, though the doubly-charged carbon atom occurs readily under certain conditions. In addition to this, the carbon atom parabola never approaches the vertical near enough to allow of its having four charges. I thought the study of the substance producing this line would be of interest, and I have for some time been working at it, and although the research is by no means completed, I have obtained some results which I should like to bring before you.

At first I was greatly hindered by not knowing the conditions under which the line occurred; although it appeared from time to time on the plates, its appearance was always fortuitous and sometimes for weeks together the plates would not show a trace of the line. The line sometimes appeared, but why it did so was a mystery, and I could not get it when I wanted it. I began an investigation, which proved long and tedious, to find the conditions under which the line appeared. I tried filling the discharge vessel with all the gases and vapors described in the books on chemistry without success. At last I tried bombarding various substances with cathode rays. Under this treatment the substances give off considerable quantities of gas, the greater part of which is hydrogen, carbonic acid or carbon monoxide. When I came to analyze by the positive rays the gases given off in this way, I found that with a large number of substances these gases contained the substances giving the three lines, so that I was now in a position to get this line whenever I wanted it, and investigate the properties of the gas to which it owes its origin. The question of the gases absorbed and given off by solids is an extremely interesting one, and a considerable number of investigations have been made on it. In all these, as far as I know, the method has been to heat the solid to a high temperature, and then measure and analyze the very considerable amount of gas which is driven off by the heating. As far as I know, no experiments have been made in which the gases were driven off by bombardment with cathode rays. This treatment, however, will cause the emission of gas even when ordinary heating fails to do so.

Belloc, who has recently published[1] some interesting experiments on this subject, after spending about six months in a fruitless attempt to get a piece of iron in a state in which it would no longer give off gas when heated, came to the conclusion that, for practical purposes, a piece of iron must be regarded as an inexhaustible reservoir of gas. There are some interesting features about the emission of gas from a heated solid. If the body is kept for a long time in a vacuum at a high temperature, the emission of gas becomes too small to be detected; if after this treatment the temperature is raised considerably, there will be a further copious emission of gas, which again diminishes as the heating continues. After it has fallen to zero, all that is necessary is to raise the temperature again and you will get a fresh supply of gas; and as far as my experience goes, after you have got all the gas you can out of the solid by heating it, you have only to expose it to cathode rays to get a fresh outburst. This effect of increased temperature in renewing the stream of gas from the solid seems to me to be too large to be accounted for merely by an increase in the rate of diffusion of the absorbed gas from the interior to the surface; it seems to be more analogous to the case of the emission of the water of crystallization from some salts. There are some salts, for example, copper sulphate, which when heated lose their water of crystallization in stages; thus, if the temperature is raised to a certain value, some of the water of crystallization comes off, but the rest remains fixed, and you may keep the salt at this temperature forever without getting rid of all the water of crystallization; on raising the temperature, however, fresh water of crystallization is given off. Something of this kind seems to take place in the case of gases absorbed in metals, and there seem to be indications that there is some kind of chemical combination between the gas and the metal. This absorbed gas may influence the behavior of the substance. For example, an ordinary carbon filament gives off, when raised to a white heat, large quantities of negatively electrified corpuscles; but Pring and Parker[2] have shown that when great precautions are taken to get rid of the absorbed gas, the emission of these corpuscles falls to less than one-millionth of their previous value. It is in the gases given off by certain metals when they are bombarded by cathode rays that I have found an unfailing source of the substance, which I shall denote by X_3, giving the line corresponding to the atomic weight 3. The arrangement I have used for investigating the presence of this gas is shown in Fig. 4. A is a vessel communicating with the bulb B, in which the positive rays are produced, by two tubes, one of which is a very fine capillary tube, while the other one is five or six mm. in diameter; taps are inserted so that one or both of these vessels can be closed, and the vessels A and B isolated from each other. A is provided with a curved cathode such as are used for Röntgen ray focus tubes, and the cathode rays focus on the platform on which the substance to be bombarded is placed. [It is not absolutely necessary to focus the cathode rays in this way, but it makes the supply of the gas X_3 more copious.] After the metal or other solid to be examined has been placed on the platform, the taps between A and B being turned so as to cut off the connection between

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[1] Ann. chim. phys., [8] **18**, 569.

[2] Phil. Mag., **23**, 192.

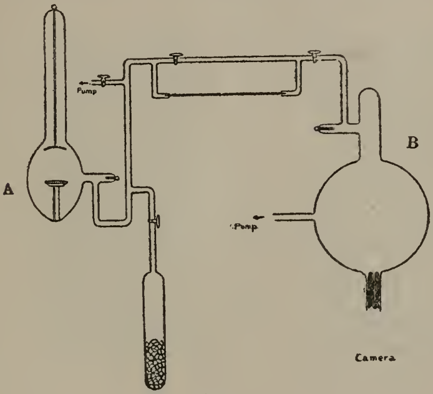
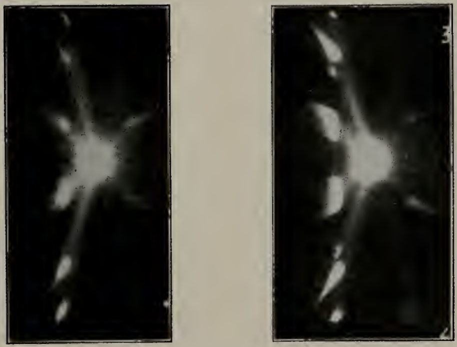


Fig. 4

them, A is exhausted until the vacuum is low enough to give the cathode rays; the discharge is then sent through A, and the cathode rays bombard the solid. The result of this is that in a few seconds so much gas, mainly carbon dioxide and hydrogen, is driven out of it that the pressure gets too high for the cathode rays to be formed, and unless some precautions to lower the pressure were taken the bombardment would stop. To avoid this, a tube containing charcoal cooled by liquid air is connected with A, and this absorbs the carbon dioxide and enough of the hydrogen to keep the vacuum in the cathode ray state. To see what new gases are given off in consequence of the bombardment, a photograph is taken while the connection between A and B is cut off. After this is finished, and when the bombardment has gone on for about four hours, the tap is turned and a little of the gas from A is allowed to go into B; another photograph is taken, and those lines in the second photograph which are not in the first represent those gases which are liberated by the bombardment, and which have escaped being absorbed by the charcoal. I have here a slide (Fig. 5) representing the result of bombarding nickel. There are two photographs, one (α) before turning the tap and the other (β) after; in the second you see the three line very distinctly, while it is absent from the first, showing that the gas giving the three line has been liberated by the bombardment. I have got similar results to these when, instead of nickel, iron, copper, lead and zinc have been bombarded. I have tried two specimens of meteorites kindly lent to me from the Mineralogical Museum, Cambridge, and found there the three line. Nearly every substance I have tried gives, the first time it is bombarded, the helium line as well as this line due to X_3; if, however, the same substance is bombarded a second time, the helium line is in general absent (occasionally it is still to be detected, though exceedingly faint); and on the third bombardment is invisible in all the substances I have tried except monazite sand, where it is given off in exceedingly large quantities as long as the bombardment continues. It is remarkable that monazite sand, which contains so many elements, gives no trace of the three line when bombarded.

I have also obtained the X_3 line and also the helium line when the tube A was replaced by one containing a Wehnelt cathode; with this the current of cathode rays through the tube was much larger than with the other cathode, though the velocity of the rays was smaller. The Wehnelt cathode gives the line without placing pieces of metal in the tube, so that in this case nothing is bombarded by the cathode rays but the glass walls of the tube; the strip of metal forming the cathode is, however, bombarded by the positive rays.

The three line, when present at all, continues even though the bombardment is very prolonged. In some cases the bombardment has been prolonged for twenty hours, and at the end of that time the line seemed almost as bright as at the beginning; indeed, I could not feel certain that there was any difference. This might lead one to suspect that X_3 was manufactured from the lead or other metal by the bombardment rather than stored up in it, and this view might be regarded as receiving some support from the fact that very little of the X_3 is liberated by heating. The following experiment is an illustration of this: I took a piece of lead, and instead of bombarding it with cathode rays I placed it in a quartz tube connected



α Fig. 5 *β*

with the vessel A, and heated the tube to a bright red heat for several hours. Large quantities of carbon dioxide and hydrogen were driven off by this process; this was absorbed by charcoal, and the residual gases, which had accumulated in A, were admitted into the vessel B; the X_3 line and helium line could just be detected, and that was all. I then gave the lead a second heating, raising this time the temperature until the quartz was on the point of softening. The lead was boiled vigorously; the heating was kept up for about three hours. In this time about three-quarters of the lead had boiled away. I then let the gases which had been given off at the second heating into the vessel B, and took another photograph; no trace of the line due to X_3 or helium could be detected. The fraction of the lead which had not been boiled away was now placed in A and bombarded by cathode rays. It now gave the three line quite distinctly; the helium line was visible, but faint. By the bombardment with the cathode rays the lead was only just melted, so that the average temperature was much less than when it was heated in the quartz tube. This rather suggests that the X_3 might be due to a kind of dissociation of the metal by the cathode rays, and not to a liberation of a store of that substance. Another experiment shows, however, that for lead, at any rate, this view is not tenable. I took some lead which had just been deposited from a solution of lead acetate by putting a piece of zinc into the solution, and forming the well-known lead tree. When I bombarded this freshly precipitated lead, I could get no trace of X_3 line; the helium line, too, was absent. I then tried another experiment. I took a piece of lead and divided it into two parts. The first of these I bombarded by the cathode rays: it gave the X_3 line quite distinctly. The other part I dissolved in boiling nitric acid, getting lead nitrate. The nitrate was heated and converted into oxide, and this was bombarded by the cathode rays: it did not give the X_3 line, showing that the X_3 is not produced by the bombardment, but is something stored up in the lead, which can be detached from it when the lead is dissolved. I have tried several samples of lead; the one which gave the X_3 line most distinctly was a piece of lead from the roof of Trinity College Chapel, several hundred years old. A sample of Kahlbaum's chemically pure lead, which must, I suppose, at no distant date have been subjected to severe ordeals by fire and water, showed the line quite distinctly, though not so well as the older lead. I have tried similar experiments with iron, and found that iron which gave the three line very distinctly ceased to do so after it had been dissolved in acid.

As the most obvious explanation of X_3 is that it is H_3, bearing the same relation to hydrogen that ozone does to oxygen, and produced in some way from the hydrogen dissolved in the metal, I tried if I could produce it by charging metals with large quantities of hydrogen, and then seeing if the hydrogen coming from the metal gave any traces of H_3. Thus, for example, I tested the hydrogen given off from hot palladium, but found no trace of X_3. I then charged nickel at a temperature of about 355° with hydrogen in the way recommended by Sabatier, but found no increase in the brightness of the X_3 over nickel that had not been deliberately exposed to hydrogen. I tried if the brightness of the line would be increased by adding hydrogen to the bulb A, in which the bombardment took place, but found no effect. I also tried adding oxygen to this bulb, thinking that if it was H_3 it would combine with the oxygen, and thus be eliminated, but no great diminution in the intensity was produced by this treatment. The gas seems quite stable, at least it can be kept for several days without suffering any diminution that can be detected; indeed, when once it has got into a bulb, there is considerable difficulty in getting the bulb free from it. It must be remembered, too, that by the method it is produced the gas is subjected all the time to electric discharges which would break it up unless it possesses very great stability. Thus if X_3 is a polymeric modification of hydrogen, it must possess the following properties:

1. It must be very stable
2. It must resist the action of oxygen
3. It must not be decomposed by long-continued exposure to the electric discharge.

These are properties which *a priori* we should hardly have expected an allotropic modification of hydrogen to possess.

Mendeléeff predicted the existence of an element with an atomic weight 3. According to him this element should be intensely electronegative and possess the properties of fluorine to an exaggerated extent. The gas X_3 can, however, be kept in glass vessels, which we should not expect to be possible if it possessed more than fluorine's power of combining with glass. I prefer to defer expressing any opinion as to the actual nature of the gas until I have had the opportunity of making further experiments upon it. It is only about two months ago that I found how to get the gas with any certainty, and, as the method involves long bombardments, each experiment takes a considerable time. This has prevented me from making several experiments which suggest themselves, and which ought to be made before coming to a final decision. I thought, however, that the investigation, though incomplete, might not be un-suitable for a Friday evening discourse, as the gas, whatever its nature, is certainly one of considerable interest, and its detection illustrates the delicacy of this new method.

SIR J. J. THOMSON

OBITUARY

LOUIS HENRY[1]

Louis Henry, the famous Belgian chemist, died at Löwen on March 9th, as the result of an apoplect c stroke which he suffered some two years earlier. He was more than 78 years old, having been born at Marche, Ardennes, on December 26, 1834. His father, an official in the Treasury Department, was frequently transferred, so that young Henry received his preparatory education in various schools. In 1851 he entered the University of Löwen and there obtained the doctor's degree in the natural sciences. After a brief stay at the University of Lüttich, with de Koninck, he went to Giessen to study under Will, the successor of Liebig. In 1858 he returned to Löwen to take charge of the Department of Mineralogy, and on the death of Prof. Marten a few years later succeeded him in the chair of Chemistry, which he retained until the beginning of his illness. In 1865 he was elected a corresponding member of the Belgian Academy of Sciences and in 1899 was awarded its prize for the most distinguished services to chemistry and physics.

Henry's name at once recalls his proof of the equivalence of the four valences of carbon. Designating the four valences by α, β, γ and δ, respectively, he prepared nitromethane, $CH_3.NO_2(\alpha)$, from silver nitrite and methyl iodide, and acetonitrile, $CH_3.CN(\alpha)$, from potassium cyanide and methyl iodide; this nitrile he hydrolyzed to acetic acid, $CH_3.COOH(\alpha)$, converted the latter into chloroacetic acid, $CH_2Cl.COOH(\alpha)$, and from this compound by the action of potassium nitrite he obtained a second nitromethane, $CH_3.NO_2(\beta)$. Again, the chloro acid, $(\beta)ClCH_2.COOH(\alpha)$, was converted into malonic acid, $CH_2(COOH)_2(\alpha,\beta)$, which, through the ethyl ester, was transformed into chloromalonic acid, $(\gamma)ClCH(COOH)_2(\alpha,\beta)$; this acid, on heating, yielded chloroacetic acid, $(\gamma)ClCH_2\text{-}COOH(\alpha \text{ or } \beta)$, which, with potassium nitrite, gave a third nitromethane, $CH_3.NO_2(\gamma)$. Finally, triethyl methanetricarboxylate, $CH(COOH)_3(\alpha,\beta,\gamma)$, obtained from the chloro acid, $(\gamma)ClCH(COOH)_2(\alpha,\beta)$, through the nitrile, gave the acid $(\delta)ClC(COOH)_3(\alpha,\beta,\gamma)$, and from this was obtained a fourth nitromethane, $CH_3.NO_2(\delta)$. Inasmuch as the four nitromethanes obtained by these methods were identical, Henry believed that the equivalence of the four valences of carbon was proved. Underlying this "proof," however, is, of course, the assumption that no migration of the atoms or groups occurs during the various reactions.

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[1] This sketch is based on a note by C. Aschman, Chem. Ztg., **37**, 765 (1913).

Henry's discovery of dipropargyl, an isomer of benzene, also attracted the widest attention, on account of its bearing on Kekulé's theories.

REVIEWS

LITERATUR-REGISTER DER ORGANISCHEN CHEMIE, geordnet nach M. M. Richters Formelsystem. Herausgegeben von der Deutschen Chemischen Gesellschaft, redigiert von ROBERT STELZNER. Erster Band, umfassend die Literaturjahre 1910 und 1911, anschliessend an die dritte Auflage von Richters Lexikon der Kohlenstoff-Verbindungen. Braunschweig: Verlag von Friedrich Vieweg und Sohn. 1913. S. xxxix + 1286. Preis: geh., M. 84; geb., M. 86.

After the preparation of the third edition of his *Lexikon*, covering all the literature abstracted in the *Chemisches Zentralblatt* up to January 1, 1910, and including some 145,000 compounds, M. M. Richter announced to the Deutsche Chemische Gesellschaft that no one man was longer able to keep up with the ever-increasing flood of literature and that he would be compelled to give up the continuation of his work. The Society then took up the matter and sent out some 4000–5000 circular letters to members and nonmembers, asking their opinion as to the feasibility of publishing a biennial continuation of the *Lexikon* under the auspices of the Society, and whether they would be willing to subscribe for such a work. The response was very encouraging, but the number of subscriptions was not large enough to justify the undertaking, especially as the Society's resources were to be heavily taxed during the next few years by the forthcoming publication of the fourth edition of *Beilstein*. At this stage, with that spirit of coöperation so characteristic of German chemical manufacturers, the firm of Leopold Cassella & Co., Frankfurt am Main, contributed 60,000 marks, to be paid in three yearly installments, and as the result we have the present volume before us.

The work involved in the preparation of this book is truly appalling. The editor is Dr. Robert Stelzner, who, since 1897, has prepared the annual index of the *Berichte* and is thus peculiarly qualified for this kind of work. The compounds are arranged according to their empirical formulas as in Richter's *Lexikon*, but the present book is much fuller than the

Lexikon, especially as regards the more common compounds which, in the *Lexikon*, are designated as "Verbindungen mit bedeutender Literatur," with a single reference to *Beilstein*. In this *Literatur-Register*, on the contrary, after every compound treated are given the melting, solidifying, decomposition and boiling points (if newly determined within the period under consideration), then the references with as much text as will serve to briefly characterize the material content of the article referred to. These references are divided into the following groups: I. *Constitution and Configuration*. II. *Occurrence* (isolation, detection), *Preparation* (purification), *Methods of Formation*. III. *Physical Properties* and *Reactions* (influence on the properties of other substances) (*a*) of the substance itself and (*b*) when mixed with other substances: (1) Solidification, melting, decomposition and boiling points; 2. Molecular weight, cryoscopic and ebullioscopic behavior; 3. Density, expansion coefficient and other constants in the field of mechanics; 4. Optical behavior; 5. Thermochemical behavior; 6. Magnetochemical behavior; 7. Electrochemical behavior; 8. Solubility, behavior as solvent, partition between solvents. IV. *Chemical Behavior* (reactions, transformations) (*a*) towards inorganic substances, (*b*) towards organic compounds. V. *Physiological Behavior*. VI. *Determination* (analysis, separation). VII. *Use and Applications*. VIII. *Salts, Esters, Compounds with Other Substances*. As a single example of the magnitude of the work, it may be stated that under Acetic Acid are given some 425 references (not including the methyl and ethyl esters). In all, about 22,000 compounds are listed, with nearly 60,000 references. And this covers only two years!

From 22 of the more important journals and the *Deutsche Reichs-Patente*, the references have been prepared from the original articles and the corresponding *Chemisches Zentralblatt* reference added; for all other journals, the *Zentralblatt* has been followed.

The system of nomenclature used is a modified form of Richter's; the difficulties encountered by the editor in this connection again draw attention to our crying need for some uniform system. Dr. Stelzner also justly deplores the custom of publishing the same articles in more than one journal, and, which is even more serious, the carelessness of some authors in checking up formulas in reading proof and their failure, often, to indicate clearly what compounds they are working with. To quote from the Introduction: "We note with astonishment, for example, that some physical constant for 'xylene' is given to many places of decimals without the author indicating whether it is *o*-, *m*- or *p*-xylene. These cases gradually accumulated to such an extent in the course of the work that the editor, for lack of time, finally had to give up the attempt to clear up the matter by an inquiry to the author—especially as this attempt was often found to fail because the result of the inquiry brought only the admission that the author himself did not know with what isomer he had worked."

At the end of the volume is printed an alphabetical list of a large number of the common names of the substances treated in the body of the book, with their empirical formulas; structural formulas of the parent substances of the cyclic compounds; and such natural substances, biochemical products, etc., as have been dealt with during the period under review but which could not be incorporated in the *Register* because their composition is not known and which must therefore be looked up in the subject index of the *Zentralblatt*.

The book is indispensable in every organic laboratory and it is to be hoped that every chemist will coöperate with the editor and his staff in their tremendously difficult undertaking by complying in his publications with the three or four simple requests that they make; *viz*., to check up all empirical and constitutional formulas, to indicate clearly the nature and position of all substituents in the compounds he is dealing with, and, in the case of stereoisomeric or optically isomeric compounds, whether they are *cis* or *trans*, dextro, levo, or racemic, and, when working with compounds of more or less uncertain composition, to point out either what is the more probably correct formula or that the composition is not yet established.

C. A. R.

TREATISE ON GENERAL AND INDUSTRIAL ORGANIC CHEMISTRY. By DR. ETTORE MOLINARI. Professor of Industrial Chemistry to the Society for the Encouragement of Arts and Manufactures and of Merceology at the Luigi Bocconi Commercial University, Milan. Translated from the second enlarged and revised Italian edition by THOMAS H. POPE, B.Sc., A.C.G.I., F.I.C., School of Malting and Brewing, University of Birmingham. With 506 illustrations. Philadelphia: P. Blakiston's Son & Co. 1913. pp. xix + 770. Price. $6.00.

The appearance of the first and second Italian editions of this unique book has already been noted in THIS JOURNAL.[1] English-speaking chemists will be sure to welcome the present translation. Mr. Pope has made a number of alterations and additions, consisting principally in amplifications of the statistical data referring to Great Britain and the United States. The translation reads smoothly and the work of the printer and binder has been well done.

C. A. R.

[1] Vol. 44, p. 202; Vol. 49, p. 73.

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A QUANTITATIVE STUDY OF ABSORPTION SPECTRA BY MEANS OF THE RADIOMICROMETER

BY J. SAM GUY AND HARRY C. JONES

(This is a continuation of the investigation which has been in progress in this laboratory for the past eight years on the absorption spectra of solutions, aided by grants generously awarded by the Carnegie Institution of Washington to H. C. Jones. This paper contains Chapter VI of Publication of the Carnegie Institution of Washington No. 190.)

The earlier work on the absorption spectra of solutions carried out in this laboratory by Jones and Uhler,[1] Jones and Anderson,[2] and Jones and Strong,[3] in connection with the nature of solution, has been briefly reviewed.[4]

A very small part of the more recent results obtained by Jones and Strong[5] has also been discussed.[6]

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[1] Carnegie Institution of Washington, Publication No. **60**; THIS JOURNAL, **37**, 126, 207 (1907).

[2] Carnegie Institution of Washington, Publication No. **110**; THIS JOURNAL, **41**, 163, 276 (1909).

[3] Carnegie Institution of Washington, Publication No. **130**; THIS JOURNAL, **43**, 37, 97, 224 (1910).

[4] Z. physik. Chem., **74**, 325 (1910).

[5] Carnegie Institution of Washington, Publication No. **160**; THIS JOURNAL, **45**, 1, 36, 113 (1911); **47**, 27, 126 (1912).

[6] Z. physik. Chem., **80**, 361 (1912).

We[1] have extended the work of Jones and Strong on the absorption spectra of solutions at high temperatures. The closed apparatus devised by Jones and Strong was used. It consisted of a gold-plated brass tube, closed at the ends by glass windows, and these were held in place by suitable screw heads. The absorption spectra of a fairly large number of aqueous solutions were studied up to 200°. The absorption bands of salts of neodymium become more diffuse with rise in temperature. The two bands λ4275 and λ5800 widen rapidly with rise in temperature, the widening being almost entirely towards the longer wave lengths. The absorption spectra of salts of praseodymium were only slightly affected by change in temperature. In the more concentrated solutions all of the bands are slightly widened, there being no appreciable change in the more dilute solutions. The absorption bands of uranyl salts nearly all widened with rise in temperature, the widening being especially pronounced towards the red. Several bands had their centers shifted as much as 15 Å. U. towards the red.

We also studied the effect of dilution on the absorption spectra of solutions. The earlier work of Jones and Anderson and Jones and Strong had shown that if dilution has any effect on the absorption spectra of solutions, it is in many cases very slight. Especially devised apparatus must, therefore, be constructed to test this effect.

The most concentrated solution used was placed in a cell whose depth was 0.5 cm. This solution was then diluted one hundred times and placed in a cell whose depth was 50 cm. The second solution was then diluted five times, and the light sent through a layer whose length was 250 cm. In this way a constant amount of absorbing matter was, in all three cases, kept in the path of the beam of light. The dissociation of the most concentrated solution was greatly increased with an increase in dilution of five hundred times. By comparing the spectrograms for the three concentrations of any given substance, we could see what effect increase in ionization or increase in hydration had on the absorption spectra.

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[1] Carnegie Institution of Washington, Publication No. **190**; THIS JOURNAL, **49**, 1 (1913).

The neodymium band, λ5800, widened about 60 Å. U. in the most concentrated solution, the widening being towards the red end of the spectrum. The widening of the double band λ5150 is symmetrical towards both ends of the spectrum.

Rise in temperature and concentrating the solution produce the same effect on bands λ4275 and λ5800. These bands are widened. Band λ5100 is changed by dilution but not by temperature. This would indicate that this band was due to molecules, which, with dilution, are broken down into ions. The bands λ4275 and λ5800, being affected in the same way by temperature and concentration, probably have to do with the hydrated molecules, since both of these influences would simplify the hydrates.

The λ5100 band is not appreciably affected by temperature, but is affected by change in dilution. This band is widest in the most concentrated solution. Since temperature has little or no effect on this band, hydration can have nothing to do with it. This band, widening as the number of molecules is increased, would indicate that it was produced by the unhydrated molecules. The remaining neodymium bands are affected neither by temperature nor dilution. They are, therefore, associated with the atoms or ions.

THE RADIOMICROMETER

The radiomicrometer used in this work consisted of a loop of thin copper wire suspended in a magnetic field. The greatest difficulty in building the radiomicrometer was to secure copper wire free from magnetic metals. If the copper contained magnetic impurities there resulted a "magnetic control" which destroyed the sensitiveness of the instrument. The best copper wire was secured from Leeds & Northrup, of Philadelphia, and from R. W. Paul, of London. The outside of the wire was dissolved away in nitric acid, to remove any iron adhering from the die in which the wire was drawn.

The alloys used in making the thermoelectric junction consisted, the one of ninety parts bismuth and ten parts tin, and the other of ninety-seven parts bismuth and three parts antimony. The method of soldering the alloys to one another and to the loop of copper wire we owe to Professor A. H. Pfund.[1] A light glass rod was attached to the end of the loop of copper wire opposite the thermal junction. This carries the mirror and the whole is suspended by means of a quartz fiber. The entire system weighed about 20 mg. and was so suspended that the loop of copper wire hung between the poles of a strong magnet. The entire system was suspended in a glass tube closed at the top by a ground-glass stopper and provided with suitable windows for exposing the junction and observing the mirror. The ground-glass stopper, from which the whole system was suspended, could be turned and the loop made to occupy any desired position relative to the magnet. The whole apparatus was packed in cotton, only the junction being exposed to the radiation.

The radiomicrometer which we built had a whole period of eight seconds. A candle placed at a distance of a meter gave a deflection of *15* cm., the light being allowed to fall on the thermal junction after passing through a glass window. When this radiomicrometer was suspended in a vacuum a candle at a distance of a meter gave a deflection of 50 cm. Since glass absorbs about half of the energy emitted by a candle, if our radiomicrometer had been provided with a rock-salt window and exhausted, a candle placed at a distance of a meter would give a deflection of *100* cm.

The "magnetic control," due to traces of magnetic impurities in the best copper wire, was, of course, greater the more sensitive the instrument. We, therefore, did not use our radiomicrometer in a vacuum. The quartz fiber was so chosen that a candle at a meter distance gave a deflection of 16 cm. The instrument had a whole period of 8 seconds, and this was sufficient sensibility for all wave lengths greater than λ4500. The measurements could thus be quickly made, and the magnetic disturbance was negligible.

When the source of the energy was removed the instrument returned to its original zero to within 0.5 mm. Repeated readings agreed to within one per cent. The source of energy was a Nernst glower, attached to a storage battery, having a voltage of 110 and an amperage of 1.2. This was found to be very constant. An ammeter was, however, kept in the circuit.

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[1] Physic. Rev., **34**, 228 (1912); Physik. Z., **13**, 870 (1912).

The details of the manipulation have already been described.[1] The light, after passing through the solution and the slit of the spectroscope, fell upon the prism of the Hilger spectroscope. A second slit was inserted in the spectroscope instead of the eye-piece. The light passed from the prism through this second slit, and was then focused on the thermal junction of the radiomicrometer. The Hilger spectroscope contained a milled head, graduated so that the wave lengths could be read off directly. By suitably turning this head any desired wave length could be thrown upon the junction of the radiomicrometer.

The first problem that was studied by means of the radiomicrometer was the *effect of dilution* on the absorption spectra of solutions. The concentration of the solution was varied, and the depth of layer of the solution through which the light passed was varied to the same extent, so that the concentration, n, times the depth of layer, d, remains constant:

$$nd = \text{constant}$$

If the solvent plays no role in the absorption of light, the absorption curves for the different concentrations of any given substance must fall directly over one another, since the number of absorbers in the path of the beam of light is kept constant.

An examination of the transmission curves for neodymium chloride shows that the more concentrated the solution the less the transparency and the *broader* the absorption bands. In the more dilute solution the *intensity* of the bands is, however, greater; and with increase in dilution the middle of the band is displaced towards the region of greater wave length.

Similar relations were found for neodymium bromide and neodymium nitrate; with increasing dilution the intensities of the bands increase, and the centers are displaced somewhat towards the longer wave length. Neodymium sulphate and acetate were also studied by means of the radiomicrometer. The absorption of the acetate is much greater than that of any other neodymium salt thus far studied, which agrees with the results obtained earlier by means of the grating spectroscope and the photographic plate.

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[1] Physik. Z., **13**, 649 (1912); This Journal, **49**, 31 (1913).

The advantage of the radiomicrometer over the grating spectroscope is that it enables us to measure not only the positions of the bands, but their intensities and the different intensities of different parts of the same band. It further enables us to work over a much greater range of wave lengths. The photographic plate is sensitive only as far as λ7600, while the radiomicrometer can be used to λ20000 or even to λ30000.

THE ABSORPTION OF LIGHT BY COMBINED WATER DIFFERENT FROM THAT OF FREE WATER

The second problem which was attacked by the radiomicrometric method is indicated by the above heading.[1] The absorption spectra of a large number of salts of different metals were being studied at the beginning of the present academic year. These spectra were compared with the absorption of water, using the same depths of water as the water in the various solutions. The depth of water in the solution was determined from its concentration and its specific gravity. It was found that the absorption of the solution was *less* than that of a layer of water having a depth equal to the depth of the water in the solution. This observation at first surprised us. We had assumed up to this time that in an aqueous solution the water present absorbed just as much as an equal layer of pure, uncombined water. The above observation showed that this assumption was absolutely wrong. We could now no longer measure the absorption of a solution, subtract the absorption of water and conclude that the remainder was the absorption due to the dissolved substance, since the water in the solution has different absorption from an equal thickness of pure, uncombined water.

We then studied the absorption spectra of a number of substances, in cells whose depths could be easily and accurately adjusted. We then measured the absorption spectra of water having the same depths of layer as the water in the solutions. We found that for certain substances the pure water was more opaque than the solutions, and for other substances the water was more transparent.

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[1] This Journal, **49**, 265 (1913).

It was soon noted that solutions of those substances which are *largely hydrated* are more transparent than pure water having the depths of the water in the solution. Aqueous solutions of *nonhydrated* or only *slightly hydrated substances*, provided the substances themselves do not absorb light, are not more transparent than pure water having the same depths as the water in the solution. This would indicate that *water combined with the dissolved substance had less absorption of light than pure, uncombined water.*

The object of the second line of work with the radiomicrometer was to test this point. The details of this work have already been published. For these, reference must be had to the earlier publications.[1]

An examination of the results for potassium chloride, ammonium chloride and ammonium nitrate, i. e., for those substances which combine with very little water, shows that for all of the wave lengths studied, the solution and water of the same depth as the water in the solution have practically the same transmission. The dissolved substance does not combine with the solvent water, and the water in the solution has almost exactly the same effect upon light as so much pure water would have. This is exactly what would be expected from our knowledge of the absorption of light by dissolved substances and by the solvent.

The results for calcium chloride, magnesium chloride and aluminium sulphate, i. e., for salts which, in aqueous solution, are strongly hydrated, show that the *solution is often more transparent than the same amount of water that is contained in the solution.*

The greater transparency of the solution as compared with the water in the solution must be due to some action of the dissolved substance on the solvent water. The important question is, what is this action?

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[1] Physik. Z., **14**, 278 (1913); THIS JOURNAL, **49**, 265 (1913); Chem. News, **108**, 25, 37 (1913).

Our earlier work on the absorption spectra of solutions has shown that the solvent can have a marked effect on the power of the dissolved substance to absorb light. This was first demonstrated by Jones and Anderson,[1] who found that neodymium chloride dissolved in water had very different absorption from neodymium chloride dissolved in methyl alcohol. A large number of examples, illustrating the same point, have since been found by Jones and Strong.[2] We interpreted the effect of the solvent on the power of the dissolved substance to absorb light as due to a combination between a part of the liquid present and the dissolved substance. This enabled us to explain a large number of facts that were brought to light by the investigations that have been carried on in this laboratory, and which do not seem to admit of any other explanation. In a word, the solvate theory of solution, as proposed by Jones[3] fourteen years ago to supplement the theory of electrolytic dissociation in order that we might have a theory of the real solutions that we use in the laboratory, and not simply a theory of ideal solutions, as the theory of electrolytic dissociation alone must be regarded, has served a good purpose in explaining the phenomena that have been previously observed in connection with the absorption of light by solutions.

We are inclined to explain the phenomena recorded in this paper by means of the same theory. For solutions of those substances which have been shown by entirely different methods not to hydrate to any appreciable extent, the absorption of light by the solution and by a layer of water equal in depth to that of the water in the solution is, to within almost the limit of experimental error, the same.

For those substances which have been shown to form complex hydrates, however, the absorption of light by their solutions and by a layer of water equal in depth to that of the water in the solution is very different. The water in these solutions is usually more opaque to light than the solution, or, what is the same thing in other words, a solution is more transparent than the water that is present in the solution.

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[1] Z. physik. Chem., **74**, 359 (1910); Carnegie Institution of Washington, Publication No. **110**.

[2] Carnegie Institution of Washington, Publications Nos. **130** and **160**; Z. physik. Chem., **74**, 68 (1910); **80**, 361 (1912).

[3] THIS JOURNAL, **23**, 89 (1900).

The most rational explanation of this phenomenon appears to us to be that the part of the water that is combined with the dissolved substance has a smaller power to absorb light than pure, free, uncombined water. The fact that we are able to detect the difference between the water in the solution and pure water, by its action on light, we regard as good evidence in favor of the water in the solution being different from pure, free water. This difference, it seems to us, can be readily accounted for by the fact that a part of the water present in the solution is in combination with the dissolved substance.

ABSORPTION SPECTRA OF A NUMBER OF SALTS AS MEASURED BY MEANS OF THE RADIOMICROMETER

The results already published, which are concerned with the energy measurements of the absorption spectra of solutions by means of the radiomicrometer, were obtained by comparing the intensity of a given source of light (after passing through the solution) with the intensity of the same source of light after passing through an equal depth of water. In a word, the depths of cells in each case were the same. As has already been stated, a cell whose depth was 1 cm. was filled with the solution and placed in the path of the beam of light and the deflection of the instrument noted; then a cell of the same depth was filled with the solvent and interposed in exactly the same position as the former cell, and the deflection of the instrument again noted. Denoting the former by I and the latter by I_0 we get the ratio I/I_0, which represents the percentage transmission of the solution as compared with water. Such a procedure was repeated at frequent intervals throughout the spectrum, locating a series of points through which the transmission curves could be drawn.

Certain phenomena presented themselves throughout the course of this investigation, which suggested a more careful study of some of the absorption bands located in the infrared portion of the spectrum; and at the same time it was thought advisable to map the absorption spectra of some of the more common salts of cobalt, nickel, etc., in terms of Beer's law, since up to the time of this investigation no quantitative study of the infrared spectrum of these salts had appeared.

In order to make a careful study of the exact intensity of the various portions of any given bands, it is clear that we are dealing with a much more complex and intricate problem than simply with the location of the band; and on this account it was necessary to improve our apparatus and at the same time to exert more care, if possible, in carrying out any given operation.

It was early found that if we desired to study that region of the infrared spectrum in which water had considerable absorption, we must not compare our solutions with an equal depth of layer of water, as noted above, but with a depth of layer equal to the water in the solution, which in the most concentrated solutions was much less than the actual depth of the cell containing the solution—a part of the cell's depth being occupied by the dissolved substance. Even when such a correction was made, it was found that for a given wave length in the water absorption bands, the solution gave greater deflections than did the solvent, i. e., that in such regions the solution was actually more transparent than an equivalent depth of water.

Remembering that the solutions with which we were then working, i. e., solutions of salts of neodymium and praseodymium, were strongly hydrated, it was thought that in view of the fact that at least a part, and in the concentrated solutions a considerable part, of the water present was there as water of hydration, it would be advisable to study the effect of colorless hydrated salts upon the absorption of water.

This chapter of our work has been sufficiently discussed elsewhere, and will be taken up here only to state that these experiments showed clearly that there were many variables to be considered. We have, first, the effect of the solvent on the absorption of the solute; and, secondly, the effect of the solute upon the absorption of the solvent. In addition to these, there was, of course, the absorption of the solvent and the solute independently. Such being the case, we would not be obtaining comparable results for various dilutions of any solutions in terms of Beer's law, even if we did compare each dilution with an equivalent amount of water. It is clear that by so doing we would not be getting comparable ratios, since the solvent and the solute were mutually affecting each other's absorption; and this effect would not be the same for the different dilutions of the same salt.

Mode of Procedure

It is, however, possible to get the exact transmission of a given depth of solution by a method of differentiation. If we placed in cell A 11 mm. of a solution and in cell B 1 mm. of the same solution, the ratio representing the respective deflections of the instrument, when these cells are alternately placed in the path of the beam of light, should give the absorption or transmission of (11 — 1) or 10 mm. of the solution.

Since, if we let A be the percentage absorption of a unit's depth of layer of the solution, and I_0 the initial intensity of the light impinging upon the surface of the source, we get:

AI_0 = amount of light absorbed by first unit layer of the solution. Then,

$I_0 - I_0A = I_0(1 - A)$ = light incident upon surface of second unit layer.

Denoting this by I_1, we get

$$I_1 = I_0 - I_0A = I_0(1 - A) \text{ or } I_1/I_0 = 1 - A$$

Considering again the third unit layer, we get, by similar reasoning,

$I_1 - I_1A$ = amount of light incident upon its surface.

Denoting this by I_2 we get

$$I_2 = I_1 - I_1A = I_1(1 - A)$$

but $I_1 = I_0(1 - A)$; therefore, $I_2 = I_0(1 - A)^2$; hence $I_n = I_0(1 - A)^n$.

We can then, by this process, obtain transmissions for given depths of solutions and for varying concentrations. This was the method adopted throughout this chapter of the work.

Description of Cells Used

In all cases where we were dealing with different depths of layer, it was necessary to use cells adjustable in length. A very satisfactory form of cell was devised and used throughout the latter part of this work. It consisted essentially of two brass cylinders telescoping neatly into each other. The external diameter of the outside cylinder was about 2.5 inches, and the thickness of the walls was in every case about 2 mm., which was sufficient to withstand handling without danger of changing the shape of the cell.

Into the ends of each cylinder there was sealed, by means of Wood's metal, a glass plate about 1 mm. thick and made of the very best optical glass. In all cases the glass plates were so nearly parallel that they showed interference fringes; and both cells gave the same deflections, either when empty or filled with the same solution and placed in the path of the light before the radiomicrometer.

After adjusting the glass ends and fixing them securely by means of Wood's metal, the entire cell was first plated with silver, being taken out of the plating bath from time to time and polished to a bright surface with the finest crocus paper. On top of this silver coating a heavy plating of gold was deposited. The distance between the glass plates fastened to the ends of the telescoping cylinders, which determined the depth of layer of solution used, was in all cases fixed by gold-plated washers, whose thickness had been accurately measured to 0.001 inch by means of a vernier caliper.

Before any series of readings was made, the positions of the two cells were so adjusted in the sliding carriage as to give equal deflections, when alternately placed in the same position before the radiomicrometer, in that portion of the spectrum where neither the solute nor solvent had any absorption; and from time to time throughout the experiment duplicate readings were made on this point to see that the cells had not changed their relative positions. In case any change was noted, a duplicate series of readings was always made. Such readings upon the same cell usually agreed to about one division of the scale, which corresponded to about 1 to 2 per cent., depending upon the throw of the instrument. In the midst of the very intense absorption bands, where the deflections of the instrument were small, reaching zero at many points, the error resulting from any drift in the instrument of reading of the scale was greater than the mean error given above.

In nearly all cases new solutions were made up and the results duplicated, so that the tables and curves below represent a mean of several series of readings. In most cases the agreement was very satisfactory, usually the difference not being over 3 per cent.

Since any change in the position of the prism was a determining factor in the portion of the spectrum which fell upon the thermo-junction, and since in the very intense, sharp bands of the neodymium salts any slight change in the position of the prism would make a great difference in the final results, great care had to be exerted in setting the head reading of the spectroscope. A change of one division on the calibrated head, which in the longer wave lengths was only about 2 mm., often made a change of 100 per cent. in the scale reading. Such difficulties were not met with in solutions where the absorption bands were broad and diffuse, as in salts of cobalt, nickel, etc.

In studying the changes which might occur in any band, it is of course necessary that all conditions be as nearly as possible the same. One of the most important factors here is that of the width of the slits of the spectroscope. With those solutions whose absorption bands are broad and diffuse, not having such well-defined edges as with the salts of neodymium and praseodymium, this is not such a determining factor. Should the band be very narrow—say approaching that of the width of the slit necessary to be used in order to secure reasonable deflections of the instrument—it is seen that any slight change in the slit will make a large difference in the amount of light falling on the thermal junction.

Considering a concrete example, let us suppose that the slit width is just equal to that of the absorption band, under a given dispersion. If, now, the band and the slit exactly coincide, it is evident that no light will be falling upon the junction, this being indicated by zero deflection of the instrument. If, on the other hand, the slit is slightly wider than the band, some light will enter around the edges of the band; and, although the narrow band may actually have complete absorption at a given point, it would not be indicated by the instrument, since some light is entering around the edges of the band.

Denoting the deflection of the instrument for a cell of 2 mm. depth of a solution of x concentration by A, and the same for 1 mm. of the same solution by B, we get, by the differential method discussed above, the ratio A/B for the intensity of the light transmitted by (2 — 1) or 1 mm. of the solution in question.

By a similar reasoning we get the ratio A'/B' for the value of the transmission of a solution of concentration $x/20$, using absorbing layers 21 mm. and 1 mm., respectively. While such a method is theoretically and mathematically correct for infinitely narrow slit widths, and practically so for bands which are wide in comparison with the necessary slit widths, yet, in the case of very sharp, narrow neodymium bands it has been found not to give comparable results. The reason for this is clearly seen in the light of the facts discussed above.

Let us consider the ratios A/B and A'/B'. In the first case we are dealing with concentrated solutions, where the absorption bands are broad; hence B is small, and, in case the slit width is comparable with the width of the absorption band, B will be very much smaller than B', since B' is only 1 mm. of an $x/20$ concentration solution. In a word, B, which is 1 mm. of the more concentrated solution, has 20 times as many absorbers as has an equal depth represented by B', and a decrease in the denominator of the fraction means an increase in its value.

While the ratios A/B and A'/B' give the transmissions for 1 mm. of a solution of concentration x, and 20 mm. of a solution of concentration $x/20$, respectively, provided the slits are narrow, yet in the visible part of the spectrum, where such wide slits had to be used on account of the small amounts of energy in this region, these ratios are not comparable.

For this reason we have confined the larger part of our work on neodymium compounds almost entirely to wave lengths greater than 0.7 μ. In all the following tables and curves representing these data, constant slit widths of 0.2 mm. have been used. This was the minimum width which could be employed in order to get reasonable deflections throughout the spectrum from 0.7 μ to 1 μ. Experiments have shown that any error resulting from slit widths would not amount to more than 3 or 4 per cent. throughout this region.

The source of light was, as in the previous work, a Nernst glower carrying about 1.2 amperes, and the current was kept constant by means of an adjustable slide-wire resistance. The source of current was a large number of storage cells, and this was never allowed to vary over 0.01 ampere. Great care was exerted in keeping the current constant while obtaining a single ratio, since this is really the only time in which a slight change in current density was dangerous.

DISCUSSION OF TABLES AND CURVES

Neodymium Chloride in Water

Table I gives the observed transmissions of solutions of neodymium chloride in water. In all the tables the following four dilutions have been studied, the depths of cell being, generally, 2.5, 5, 10, and 20 mm, respectively, and the concentrations being made so as to keep $n \times d = k$. In column 1 of each table there is given λ, taken at such intervals as the solution in question required. In those portions of the spectrum where the transmission was complete, or very nearly so, these intervals were greater than in those regions where there were absorption bands.

Reading from left to right in this table, beginning with column 2, there are given the absorptions for solutions of the following concentrations: 2.141, 1.07, 0.535, and 0.267 normal, respectively, the corresponding depths of absorbing layer being 2.5, 5, 10 and 20 mm., respectively. In every case the transmission was obtained from the ratio $(x + 1)/1$, where x is 2.5, 5, 10 and 20 mm., respectively.

In all cases the concentrated mother solution was carefully made up, its concentrations determined by a gravimetric precipitation of the metal, and the succeeding solutions made by diluting measured parts of the mother solution.

Observations are given here over only that portion of the infrared spectrum from λ6800 to λ10000. It is in this region that the most pronounced neodymium bands occur. It was thought advisable not to go further into the infrared, since beyond 1 μ the general absorption due to the solvent is very marked. This would, of course, interfere with a quantitative study of any band occurring in this region, since it is impossible to separate the two absorptions, previous work having shown that they are not additive.

The work in the visible region of the spectrum was limited by the slit widths necessary to be used, which has been mentioned and discussed above. We have rather chosen a limited portion of the infrared, over which we could work without altering either the intensity of the light or the slit width, which was in all cases 0.2 mm.

Table I—Percentage Transmission of Neodymium Chloride Solutions

λ	D. = 2.5 mm. C. = 2.141 N	D. = 5 mm. C. = 1.071 N	D. = 10 mm. C. = 0.535 N	D. = 20 mm. C. = 0.267 N
686	93	88	88	86
693	95	95	95	94
698	96	96	96	94
704	96	96	98	94
708	96	93	95	92
712	92	93	95	88
716	88	89	88	85
720	81	78	81	81
723	64	62	63	56
726	32	31	25	23
730	7	7	5	6
733	0	0	0	0
737	0	0	0	0
741	5	2	1	2
746	18	14	12	5
751	36	39	29	28

755	54	55	52	49
759	75	74	72	68
763	85	85	83	81
767	84	86	85	83
770	79	81	80	76
774	67	73	65	61
779	47	45	45	40
783	29	27	26	24
787	22	10	10	7
791	0	0	0	0
796	0	0	0	0
800	15	10	8	6
805	24	23	22	18
809	40	39	38	37
814	58	58	58	53
819	80	78	78	76
825	89	91	91	82
830	93	92	93	88
834	94	95	95	88
839	93	93	93	87
845	91	92	91	86
850	87	86	87	78
856	75	73	71	66
861	54	46	43	40
867	29	21	18	16
872	28	24	23	18
877	40	39	40	34
882	53	48	52	47
888	60	59	60	53
894	61	59	61	56
900	67	66	66	59
906	80	78	79	71
912	90	92	89	79
917	96	93	94	86
923	98	97	96	86
928	98	96	96	84
933	98	96	96	81
938	98	94	90	75

The curves representing this table are given in Figs. I–IV, inclusive. The percentages of transmission are plotted as ordinates, while the wave lengths are given as abscissas. An examination of these curves shows three pronounced minima, representing the three absorption bands, with their centers near λ7300, λ7950 and λ8700, and less marked bands near λ7150 and λ9000. The latter of these small bands is possibly

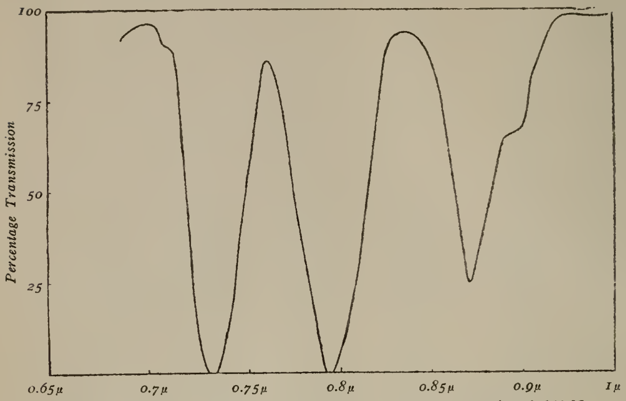

Fig. I—Neodymium Chloride. Cell depth, 2.5 mm.; concentration, 2.141 N

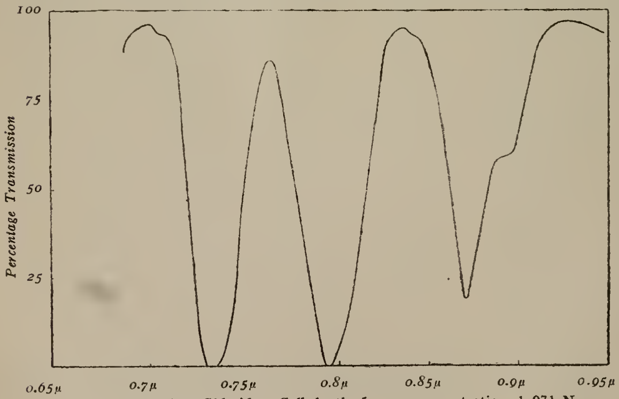

Fig. II—Neodymium Chloride. Cell depth, 5 mm.; concentration, 1.071 N

due in part to the absorption of the solvent; but since its intensity does not increase markedly with dilution, it is more probably a doublet. Considering the curves representing all four dilutions, we see that the λ7300 and λ7900 bands show complete absorption over a considerable range of wave lengths, and any change in intensity could not be very noticeable. The λ8700 band, however, has its minima gradually lowered as we pass from Fig. I to Fig. IV, i. e., in the direction of increasing dilution. This phenomenon has been noted elsewhere, and a possible explanation of it based upon a theory of resonance suggested. A closer and more exact study has shown that although the phenomenon is a real one, yet it is probable that it may in part be due to the combined effect of the slight water absorption and, even a more important factor, the slit widths, as discussed above.

The regions of maximum transmission occur near λ7600 and λ8400, and solutions of neodymium chloride become almost completely transparent beyond 1 μ, except for the general absorption of the solvent. Slight absorption bands occur in this region, one near 1.5 μ, but they are so masked by the intense water absorption that it was found impossible to make a quantitative study of them.

From a comprehensive study of the four curves representing the absorption spectra of concentrated solutions of neodymium chloride, it seems probable that Beer's law holds quantitatively for the infrared region, except for such slight changes as have been fully discussed above.

Since, as mentioned above, the absorption bands with their centers near λ7300 and λ7950, in solutions of such concentrations as are given in Table II, reach complete absorption, and as in such cases it would not be easy to detect any change in their intensity, it was thought advisable to make a study of a series of more dilute solutions of the same salt.

The results of this experiment are given in Table II. Reading from left to right, the concentrations are 0.536, 0.267, 0.133, and 0.067 normal, respectively, the corresponding depths of absorbing layers being 2.5, 5, 10, and 20 mm., respectively. Here again it is seen that the conditions of Beer's law are adhered to. The results are graphically represented in Figs. V to IX, inclusive. These curves show minima in

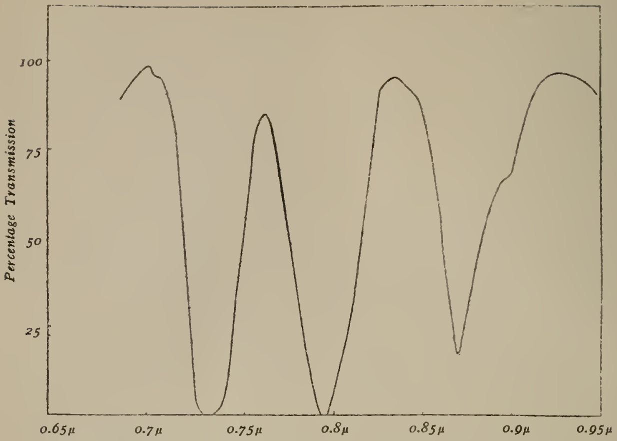

Fig. III—Neodymium Chloride. Cell depth, 10 mm.; concentration, 0.535 N

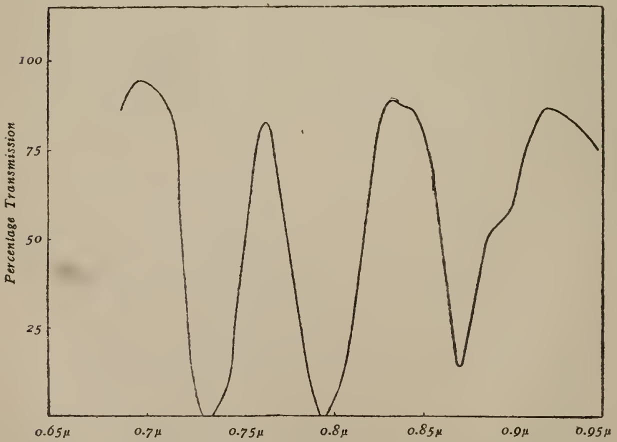

Fig. IV—Neodymium Chloride. Cell depth, 20 mm.; concentration, 0.267 N

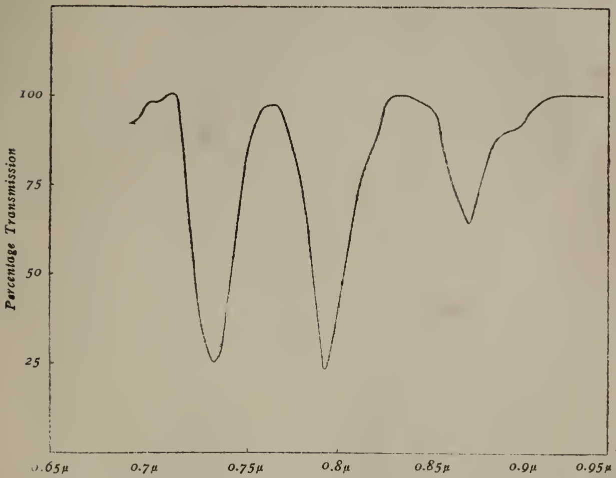

Fig. V—Neodymium Chloride. Cell depth, 2.5 mm.; concentration, 0.536 N

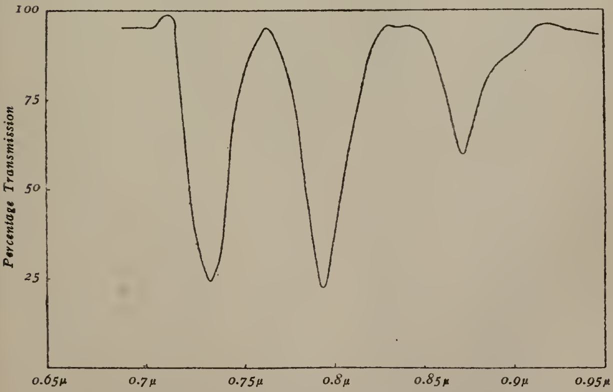

Fig. VI—Neodymium Chloride. Cell depth, 5 mm.; concentration, 0.267 N

about the same positions as did the curves representing the mere concentrated solutions, but since the solutions are more dilute, they are accordingly more transparent; hence the minima in the curves are not so pronounced. The maxima occurring near λ7300 and λ7900 are at about 25 per cent.

Table II—Transmission of Neodymium Chloride Solutions (Dilute)

λ	D. = 2.5 mm. C. = 0.536 N	D. = 5 mm. C. = 0.267 N	D. = 10 mm. C. = 0.133 N	D. = 20 mm. C. = 0.067 N
686	92	95	94	92
693	93	95	95	97
698	97	95	95	97
704	98	95	96	97
708	98	95	97	98
712	100	98	96	96
716	100	98	98	92
720	96	94	89	89
723	85	84	83	84
726	59	54	58	53
730	42	41	40	34
733	31	29	26	25
737	25	24	20	22
741	28	29	29	29
746	47	44	51	44
751	69	65	65	60
755	85	82	82	78
759	93	86	90	86
763	97	90	92	92
767	97	95	90	92
770	97	93	90	89
774	91	86	87	84
779	79	76	78	74
783	69	61	59	56
787	47	39	38	34
791	23	24	20	18
796	28	25	23	23
800	45	39	38	39
805	64	59	57	57
809	78	72	71	70
814	85	84	82	82
819	92	91	88	88
825	100	94	94	94
830	100	96	94	93
834	100	94	94	92

839	100	96	93	91
845	98	95	94	91
850	97	94	90	89
856	92	87	84	83
861	78	77	74	70
867	70	64	62	60
872	64	60	59	56
877	74	71	68	66
882	84	80	76	75
888	89	84	82	78
894	90	84	83	79
900	91	88	86	81
906	95	90	87	83
912	98	95	90	84
917	100	96	92	85
923	100	96	93	84
928	100	95	92	84
933	100	94	94	83
938	100	94	95	78

Table III—Transmission of Neodymium Nitrate Solutions

λ	D. = 2.5 mm. C. = 2.010 N	D. = 5 mm. C. = 0.15 N	D. = 10 mm. C. = 0.525 N	D. = 20 mm. C. = 0.262 N
686	86	88	85	78
693	93	96	91	89
698	93	96	93	93
704	96	94	93	91
708	95	96	96	88
712	89	90	94	89
716	84	88	88	82
720	78	79	78	78
723	80	63	61	58
726	40	33	30	28
730	14	14	10	9
733	0	0	0	0
737	0	0	0	0
741	11	4	0	0
746	12	15	6	6
751	22	23	22	17
755	38	39	40	38
759	60	60	62	55
763	75	75	74	70
767	80	80	83	79
770	75	75	79	75
774	64	66	68	62
779	47	47	48	44

(*Table III continued.*)

λ	D. = 2.5 mm. C. = 2.010 N	D. = 5 mm. C. = 0.15 N	D. = 10 mm. C. = 0.525 N	D. = 20 mm. C. = 0.262 N
783	32	32	29	26
787	16	10	13	9
791	11	8	2	5
796	0	0	0	0
800	12	10	6	6
805	21	19	14	15
809	35	33	30	30
814	49	49	47	47
819	63	67	65	64
825	79	80	79	77
830	82	88	89	82
834	92	92	93	85
939	96	94	94	89
845	92	91	91	85
850	87	84	85	77
856	76	70	72	65
861	61	57	53	47
867	43	36	35	32
872	30	27	26	22
877	31	30	28	25
882	43	42	41	36
888	55	52	51	48
894	65	60	59	61
900	68	66	66	62
906	77	75	75	67
912	86	84	83	75
917	94	90	97	83
923	98	92	90	84
933	100	96	88	86
938	100	96	83	77

The λ8700 band has a minimum transmission in regions λ7200, λ7600, λ8300 and λ9300. It will be noticed that beyond 0.9 μ all of the curves drop sharply with dilution, which is due entirely to the increasing absorption of the water.

Curves V to IX, inclusive, show just what might be anticipated from Curves I to IV, a lowering of absorption maxima as we pass towards the more dilute solutions. This change is most marked in the λ8700 band, and it is in this region that the absorption of the water is most pronounced, although a 20 mm. layer of water in this region has at no point over 10 per cent. absorption. The change in the intensity of the absorption band is greater than this amount, but it seems probable that this, together with the added correction for the slit widths, may account for the phenomenon, and that Beer's law holds for the dilute solutions of neodymium chloride.

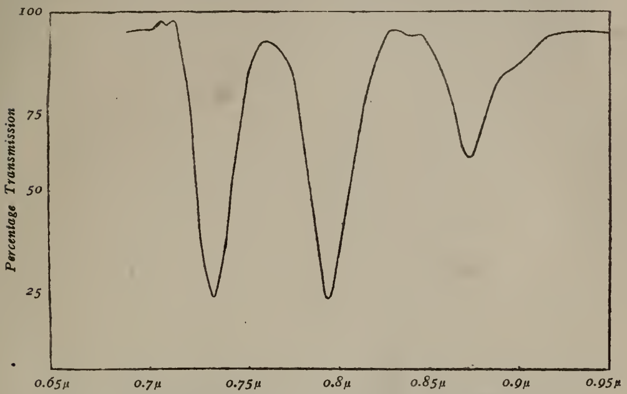

Fig. VII—Neodymium Chloride. Cell depth, 10 mm.; concentration, 0.133 N

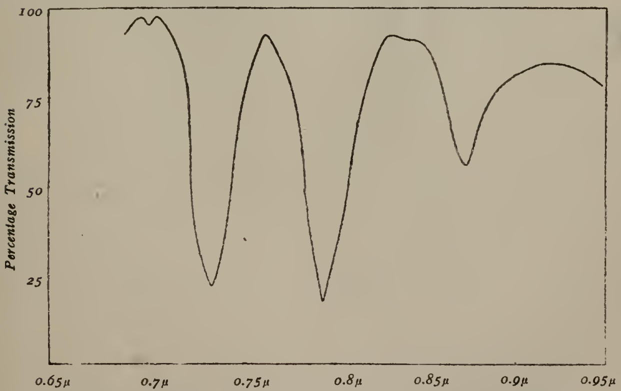

Fig. VIII—Neodymium Chloride. Cell depth, 20 mm.; concentration, 0.067 N

Neodymium Nitrate

Table III gives the percentage transmission for solutions of neodymium nitrate. Column 1 gives the respective wave

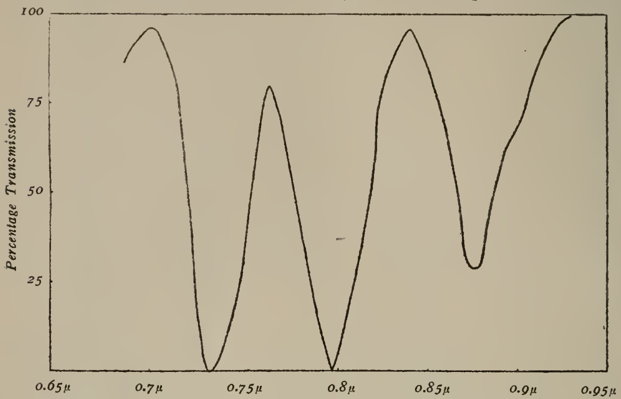

Fig. IX—Neodymium Nitrate. Cell depth, 2.5 mm.; concentration, 2.01 N

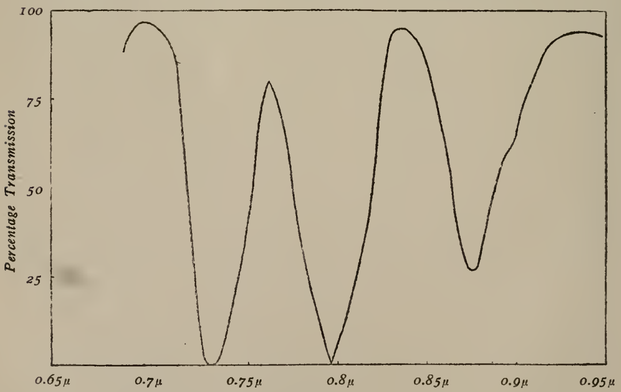

Fig. X—Neodymium Nitrate. Cell depth, 5 mm.; concentration, 1.05 N

lengths at such intervals as the solutions required. Reading from left to right, we find the percentage transmissions for the following concentrations: 2.010, 1.050, 0.525, and 0.262 normal, respectively, the corresponding depths of absorbing layers being 2.5, 5, 10, and 20 mm. Curves IX to XII, inclusive, represent these results, the abscissas being wave

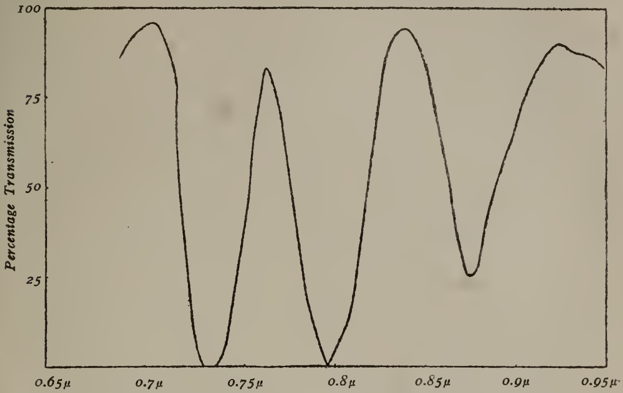

Fig. XI—Neodymium Nitrate. Cell depth, 10 mm.; concentration, 0.525 N

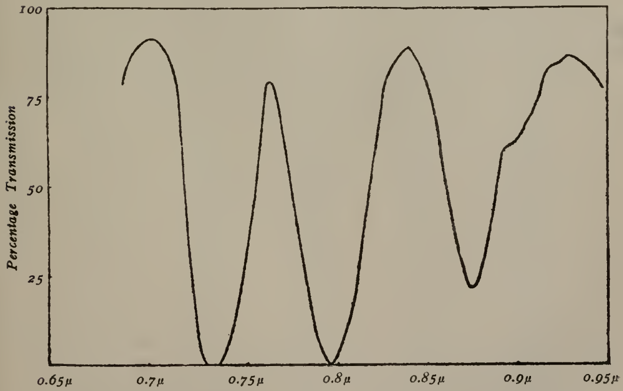

Fig. XII—Neodymium Nitrate. Cell depth, 20 mm.; concentration, 0.262 N

lengths and the percentage transmissions being given as ordinates. It is seen that the absorption bands in the nitrate solutions, as with those of the chloride discussed above, show three minima at λ7300, λ7950 and λ8750. The nitrate bands are not as intense as those of the concentrated solutions of the chloride given in Curves I to IV. This is what we should expect, since the concentrations of the nitrate solutions are not so great. However, two of the absorption bands reach zero transmission. A comparative study of any of these bands in the succeeding curves shows that, just as was found with the chloride bands, they become more intense with dilution. The decided decrease in the transmission in the regions of the spectrum beyond 1μ is undoubtedly due to the increasing absorption of water as the solution becomes more dilute. The other slight deviations from Beer's law are not greater than could be accounted for by the corrections mentioned under the discussion of the chloride curves.

Neodymium Acetate

Table IV gives the results obtained for solutions of neodymium acetate in water. The concentrations, reading from

Table IV—Transmissions of Neodymium Acetate Solutions

λ	D. = 2.5 mm. C. = 0.617 N	D. = 5 mm. C. = 0.308 N	D. = 10 mm. C. = 0.154 N	D. = 20 mm. C. = 0.077 N
686	98	97	94	94
693	92	91	93	95
698	97	97	96	93
704	98	100	92	93
708	96	98	92	96
712	100	96	94	96
716	100	94	90	94
720	94	90	90	94
723	87	87	79	76
726	69	64	60	57
730	44	36	32	30
733	22	22	18	21
737	24	17	14	15
741	30	23	22	25
746	41	39	34	35
751	52	55	52	55
755	71	71	65	67

759	81	84	81	82
763	90	91	87	88
767	93	93	89	87
770	94	90	87	89
774	89	88	83	84
779	72	74	74	75
783	62	63	59	55
787	45	40	37	32
791	24	21	17	18
796	22	17	17	14
800	27	28	27	28
805	57	46	44	46
809	69	63	62	64
814	74	76	73	75
819	90	83	83	82
825	92	89	86	87
830	92	93	92	91
834	98	98	92	91
839	96	97	94	90
845	97	97	90	88
850	95	96	90	87
856	95	94	84	83
861	91	83	77	71
867	72	69	65	67
872	62	60	56	53
877	66	67	58	57
882	71	72	66	66
888	83	82	76	75
894	87	84	81	78
900	91	88	84	79
906	92	90	87	83
912	94	90	90	82
917	96	93	89	85
923	97	96	94	86
933	99	95	91	83
938	99	95	92	77

left to right, were 0.617, 0.308, 0.154 and 0.077 normal, respectively, the corresponding depths of absorbing layer being 2.5, 5, 10 and 20 mm., respectively. The results in this table are plotted in Figs. XIII to XVI, inclusive. The percentage transmission and wave lengths are represented, respectively, by the ordinates and abscissas of the curves.

The minima of transmission fall at approximately the same

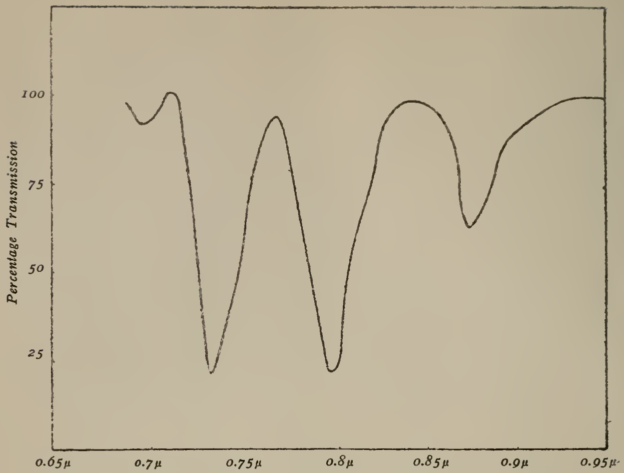

Fig. XIII—Neodymium Acetate. Cell depth, 2.5 mm.; concentration, 0.617 N

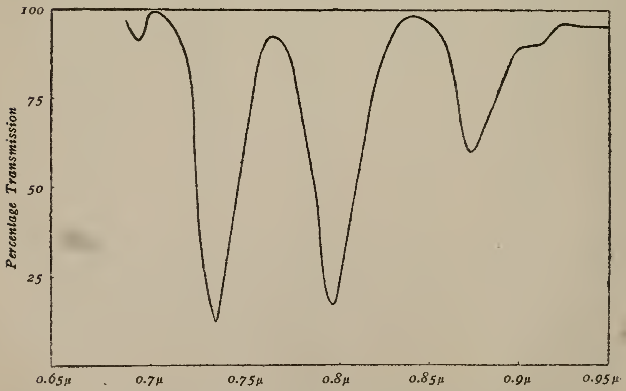

Fig. XIV—Neodymium Acetate. Cell depth, 5 mm.; concentration, 0.308 N

positions as with the chloride and nitrate solutions discussed above, i. e., at λ7300, λ7950 and λ8750. As indicated by the photographic method, the solutions of neodymium acetate have greater absorbing powers for a given concentration than either the chloride or nitrate.

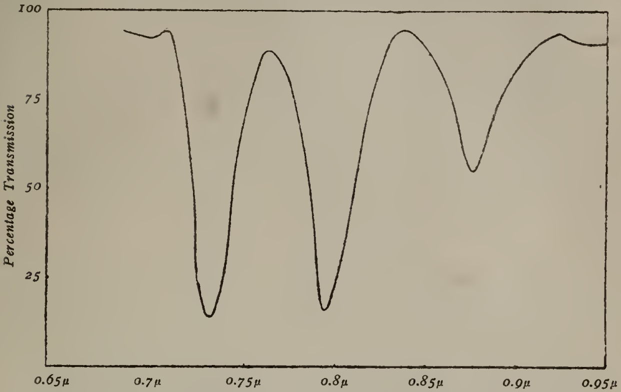

Fig. XV—Neodymium Acetate. Cell depth, 10 mm.; concentration, 0.154 N

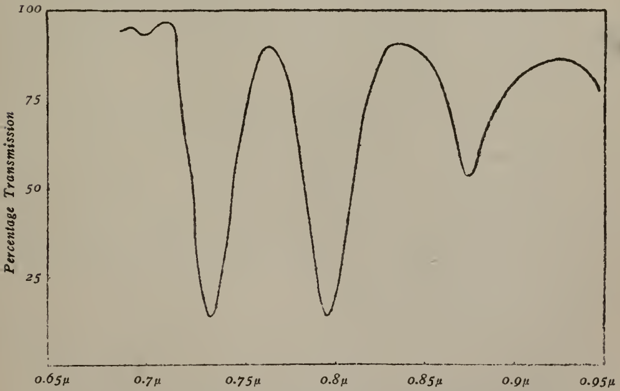

Fig. XVI—Neodymium Acetate. Cell depth, 20 mm.; concentration, 0.077 N

The small band near λ7000 appears slightly more intense with the acetate than with equal concentrations of the other salts; and the more intense bands λ7300, λ7950 and λ8750 show the same general tendency to have their minima lowered with increasing dilution. This set of curves shows in a marked way the rapid increase in the absorption near λ9500, which is due to the water present in the solution, and illustrates the difficulty that is met with when working with aqueous solutions at greater wave lengths than 1μ. Even over the range of wave lengths at which we have worked, it is seen that the absorption due to water is a disturbing factor.

Praseodymium Chloride

Solutions of praseodymium salts are not of great interest, from our standpoint, in those regions beyond the visible part of the spectrum. It was found that such solutions were transparent in the infrared end of the spectrum as far as 1.5, except two very weak bands which fall just in the midst of the intense water bands. Since, at this point, a very thin layer of water is almost completely opaque, it is evident that it would be impossible to study aqueous solutions in this region, especially dilute solutions.

As shown by the photographic plate, praseodymium salts possess two groups of bands in the visible spectrum, one in the green near λ4600 and another near λ5900. Since the amount of energy at the former wave length is so very small, the width of slits necessary to be used was too large to give satisfactory results. Such bands could, of course, be detected, but the deflections of the instrument at this part of the spectrum are very small, and, hence, relatively large errors would occur in making the readings.

For this reason we have confined our attention to a careful study of the one band which has its center near λ5900. Table V gives the observed transmissions for the four dilutions of solutions of praseodymium chloride. In column 1 there is given λ taken at such intervals as the graduated head of the spectroscope would permit. Reading from left to right, the respective concentrations were 1.377, 0.688, 0.344 and 0.177

normal, the corresponding depths of absorbing layer being 2.5, 5, 10 and 20 mm., respectively.

Table V—Percentage Transmissions of Praseodymium Chloride Solutions

λ	D. = 2.5 mm. C. = 1.377 N	D. = 5 mm. C. = 0.688 N	D. = 10 mm. C. = 0.344 N	D. = 20 mm. C. = 0.177 N
506	100	100	100	100
518	100	98	100	100
530	100	98	100	100
544	99	99	99	98
556	99	99	99	98
563	100	98	100	98
565	99	99	98	97
567	97	100	98	97
572	97	99	95	97
577	96	98	93	95
579	91	92	90	92
583	85	86	84	80
585	77	76	70	72
587	60	59	55	56
589	45	46	40	40
592	35	35	32	33
595	35	34	34	33
597	43	43	42	42
600	56	56	56	56
602	69	69	68	69
605	81	82	81	81
607	90	92	88	88
611	93	94	93	94
614	97	99	95	97
629	98	100	97	98

In terms of Beer's law, the curves representing these tables should be identical. Such curves are represented by Fig. XVII. Beginning with the curve nearest the left and proceeding towards the right, the succeeding curves represent the four dilutions of praseodymium chloride as given in the preceding paragraph.

The curve representing the most concentrated solution is nearest the left of the figure. It is seen that these curves are identical to within the limits of experimental error; the slight increase in the absorption with dilution is to be attributed to the slit width correction. The slit width was in every case 0.4 mm. Water has no absorption in this region.

The results recorded in these curves are in agreement with previous photographic results. The minimum in transmission, which in each case is about 30 per cent., occurs near λ5900. The total deviation from Beer's law over the dilution studied is not over 3 per cent., which is well within the experimental error in this portion of the spectrum.

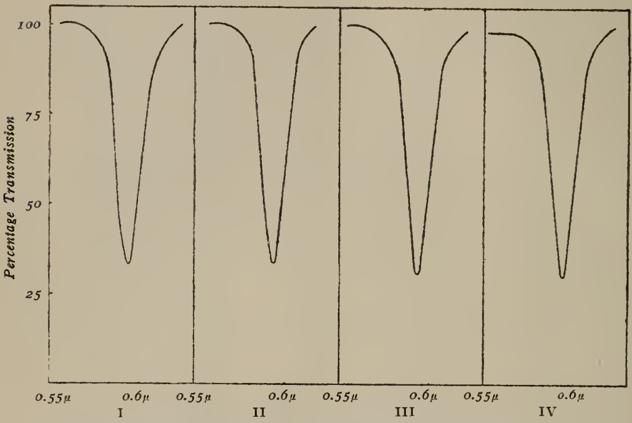

Fig. XVII—Praseodymium Chloride. I. Cell depth, 2.5 mm.; concentration, 1.377 N. II. Cell depth, 5 mm.; concentration, 0.688 N. III. Cell depth, 10 mm.; concentration, 0.344 N. IV. Cell depth, 20 mm.; concentration, 0.177 N.

Praseodymium Nitrate

Corresponding results for solutions of praseodymium nitrate are given in Table VI. The concentrations of the solutions, beginning on the left and reading towards the right, were 1.282, 0.641, 0.320 and 0.161 normal, respectively, the corresponding depths of absorbing layer being 2.5, 5, 10 and 20 mm., respectively.

Table VI—Percentage Transmissions of Praseodymium Nitrate Solutions

λ	D. = 2.5 mm. C. = 1.282 N	D. = 5 mm. C. = 0.641 N	D. = 10 mm. C. = 0.320 N	D. = 20 mm. C. = 0.160 N
506	100	100	99	100
518	98	98	100	100
530	100	100	99	99
544	99	98	100	100
556	99	98	100	98
563	99	99	98	97
565	96	100	98	96
567	98	100	98	97
572	90	97	96	95
577	93	92	94	93
579	90	92	90	91
583	83	86	85	83
585	73	74	72	72
587	62	60	60	58
589	48	46	46	45
592	40	40	38	36
595	37	36	36	36
597	44	44	44	42
600	56	56	56	54
602	68	67	68	67
605	79	82	79	80
607	87	89	89	88
611	91	92	94	92
614	95	95	97	96
629	98	98	99	98

The results are plotted in Fig. XVIII. Reading from left to right, there is shown the effect of increased dilution on solutions of praseodymium nitrate, and such concentrations and depths of absorbing layers as were mentioned above, the most concentrated solution being nearest the left of the figure.

As with the curves representing the solutions of praseodymium chloride, these curves show that Beer's law holds quantitatively for solutions of the nitrate. Neither the position nor the intensity of the band is altered more than the limits of error of our work for the range of dilution studied. It may be recalled that this is in exact agreement with the photographic results recorded elsewhere in Monograph 190 of the Carnegie Institution.

Salts of Nickel

Table VII gives the percentage transmission of the nickel salts studied. Beginning at the left of the table, column 1 gives λ, taken at such intervals as the solutions required, and reading towards the right are the results for the following salts: Nickel chloride, depth of cell 3 mm.; concentration, 2.74 normal; nickel nitrate, depth of cell 5 mm.; concentration 1.68 normal; nickel sulphate, depth of cell 5 mm.; concentration 1.108 normal, respectively.

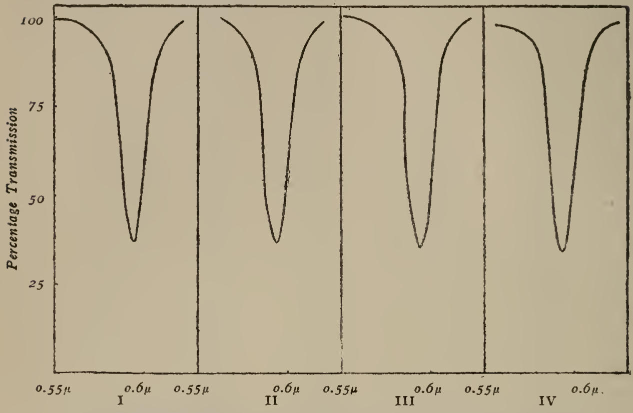

Fig. XVIII—Praseodymium Nitrate. I. Cell depth, 2.5 mm.; concentration, 1.282 N. II. Cell depth, 5 mm.; concentration, 0.641 N. III. Cell depth, 10 mm.; concentration, 0.320 N. IV. Cell depth, 20 mm.; concentration, 0.160 N.

Curves representing these results are given in Figs. XIX, XX and XXI.

Table VII—Percentage Transmissions of Solutions of Nickel Salts

λ	Nickel chloride D. = 3 mm. C. = 2.74 N	Nickel nitrate D. = 5 mm. C. = 1.68 N	Nickel sulphate D. = 5 mm. C. = 1.108 N
544	71	69	81
556	64	69	79
563	62	65	76
565	60	61	73
577	56	57	68

583	52	50	66
587	47	46	61
592	40	40	60
597	34	33	40
602	26	28	43
607	22	22	37
614	17	17	33
618	12	12	26
625	10	9	23
632	8	6	18
638	5	6	15
643	3	4	12
650	0	4	12
662	0	3	10
676	0	2	10
693	0	9	11
755	7	8	10
770	7	8	18
779	11	13	20
787	14	17	30
796	16	20	33
805	18	24	40
814	22	31	44
825	28	36	49
834	32	40	55
845	36	46	58
856	41	48	64
867	46	51	66
877	49	52	68
888	51	56	69
900	53	56	68
912	54	56	67
923	52	51	64
933	50	48	62
938	47	44	59
955	42	38	52
966	36	30	44
978	30	24	38
990	26	20	33
1002	22	16	28
1012	20	14	24
1023	15	9	22
1035	13	8	20
1047	9	4	17
1060	6	4	14

Nickel Chloride

Fig. XIX, the curve for nickel chloride, shows an increasing absorption from 70 per cent. transmission at λ5200 to complete absorption at λ6300. From this point there is complete absorption to the regions λ7200, and then a gradual increase in transmission, reaching a maximum of 53 per cent. near λ9000, then decreasing again to zero transmission at λ10000.

As has been shown photographically, the visible spectrum of salts of nickel consists of intense broad absorption bands both in the blue and red, showing a single region of transmission extending to about λ6500 in the red. It is interesting to note that by means of the radiomicrometer we are able to study another region of transmission which reaches a maximum near λ9000. From this point the absorption rapidly increases until the region of water absorption is reached. It was not possible to determine whether the solution again became transparent beyond this point, on account of the water absorption.

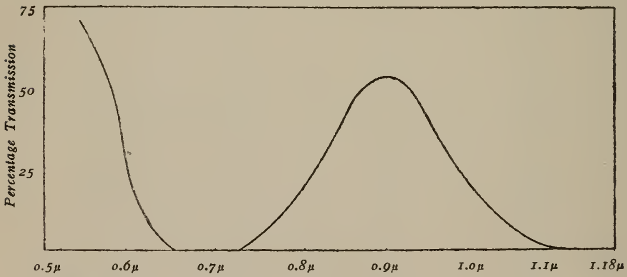

Fig. XIX—Nickel Chloride. Cell depth, 3 mm.; concentration, 2.74 N

Nickel Nitrate

Fig. XX, which represents the second column of Table VII, gives the transmission, as observed, for a solution of nickel nitrate, concentration 1.68 normal and 5 mm. absorbing layer. This figure is almost exactly analogous to the curve for nickel chloride, just discussed in the preceding paragraph, and shows maxima at λ5400 and λ9000. There is complete absorption in the region λ7000 and beyond 1.1 μ. Figs. XIX and XX represent approximately equal amounts of the chloride and nitrate, respectively, and are very similar.

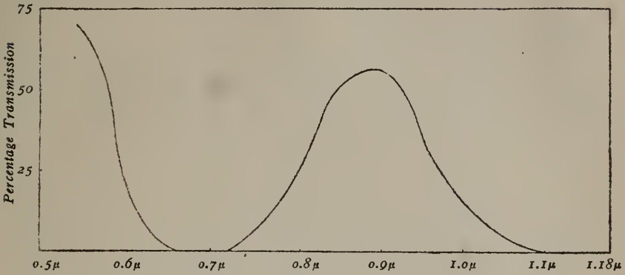

Fig. XX—Nickel Nitrate. Cell depth, 5 mm.; concentration, 1.68 N

Nickel Sulphate

The curve representing the last column of this table is given in Fig. XXI. The concentration of nickel sulphate was 1.108 normal, and the depth of absorbing layer was 5 mm.

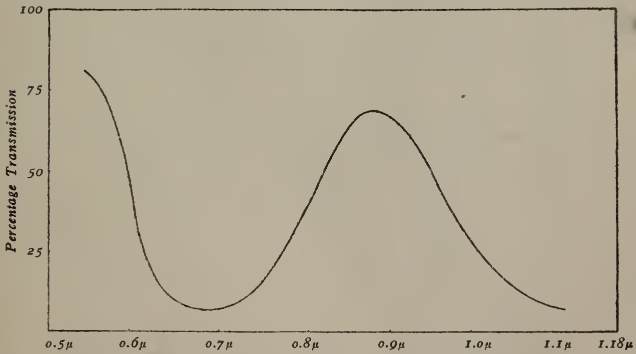

Fig. XXI—Nickel Sulphate. Cell depth, 5 mm.; concentration, 1.108 N

It will be seen that this solution is slightly more dilute than the other two solutions of nickel salts studied, and that in no region does the curve representing the transmission reach complete absorption. Maxima in transmission appear near λ5400 and λ9000 and minima of about 8 per cent. at λ6900 and λ11000. Readings were not made at greater wave lengths with any of the nickel salts, on account of the intense water absorption slightly beyond this region.

No striking or characteristic difference is noted in the absorption as shown by the three curves representing the three salts of nickel studied. Each of them shows maxima and minima in about the same region of the spectrum.

Salts of Cobalt

The photographic plate shows that in the visible region salts of cobalt have a strong ultraviolet absorption, a band in the orange near λ5000, and increasing transmission from the center of this band toward the longer wave lengths. It was interesting to see whether solutions of cobalt salts were completely transparent beyond the limit of sensibility of the photographic plate, or if such solutions again showed absorption bands in the infrared. It was also of interest to know whether equal concentrations of the different salts showed the same or different absorption bands. With this idea in view, the solutions of five salts of cobalt were studied. In each case the concentration was 0.347 normal, and the depth of absorbing layer 10 mm.

The results are given in Table VIII. Beginning at the left are given, in their respective order, the observed transmissions

Table VIII—Transmissions of Cobalt Solutions

λ	Cobalt chloride D. = 10 mm. C. = 0.347 N	Cobalt bromide D. = 10 mm. C. = 0.347 N	Cobalt nitrate D. = 10 mm. C. = 0.347 N	Cobalt sulphate D. = 10 mm. C. = 0.347 N	Cobalt acetate D. = 10 mm. C. = 0.347 N
544	12	21	20	14	15
556	19	33	31	26	31
572	39	50	35	48	53
583	48	61	64	57	59
589	59	68	68	62	69
592	63	74	73	67	72
605	68	74	77	67	72
614	70	74	77	68	74
622	72	74	79	68	75

632	72	75	84	69	76
640	72	75	76	70	77
650	73	76	79	71	76
660	73	78	81	72	80
667	74	78	82	74	83
678	79	82	85	77	84
686	80	84	88	79	85
693	81	85	90	88	88
708	84	87	91	81	89
720	84	89	91	82	92
730	85	87	92	83	89
741	88	88	88	82	91
755	87	89	89	83	91
767	87	92	89	82	92
779	88	89	89	84	90
791	90	89	89	83	90
805	91	89	87	84	89
819	88	88	84	83	90
834	87	87	83	83	86
850	88	86	76	80	86
867	88	95	95	80	85
882	84	84	82	79	83
900	84	81	77	76	84
917	83	82	79	77	82
933	78	77	79	73	78
949	70	69	70	66	70
966	58	55	56	54	56
984	51	49	50	47	52
1,002	49	48	50	47	49
1,018	51	50	50	47	52
1,035	51	50	53	50	52
1,053	48	50	56	49	52
1,072	46	46	50	44	48
1,091	41	41	46	40	41
1,109	34	35	39	34	36
1,123	29	31	35	30	32
1,136	24	25	23	24	25
1,147	17	21	14	16	19
1,162	12	12	13	11	12
1,174	9	10	11	10	10
1,187	9	9	10	9	9
1,202	8	8	9	8	10

for 10 mm. of solution of the following salts: Cobalt chloride, cobalt bromide, cobalt nitrate, cobalt sulphate and cobalt acetate.

The results of Table VIII are plotted as transmission curves in Figs. XXII to XXVI, inclusive. A study of these curves shows that they are very similar, all having maxima of transmission at the following points: λ5950, λ7800, λ9100 and λ10,600. In general, for all the salts of cobalt studied, the transmission curves rise rapidly from λ5000 to λ5900, where the transmission reaches about 65 per cent. The curves show

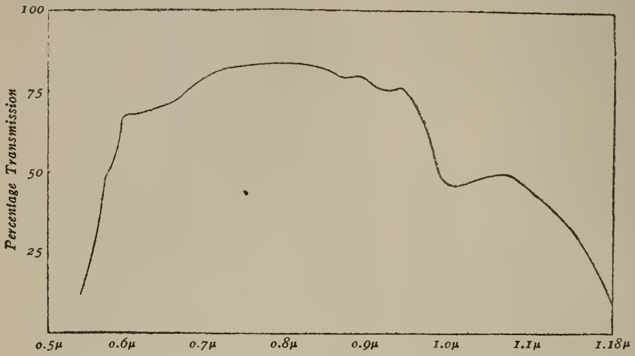

Fig. XXII—Cobalt Chloride. Cell depth, 10 mm.; concentration, 0.347 N

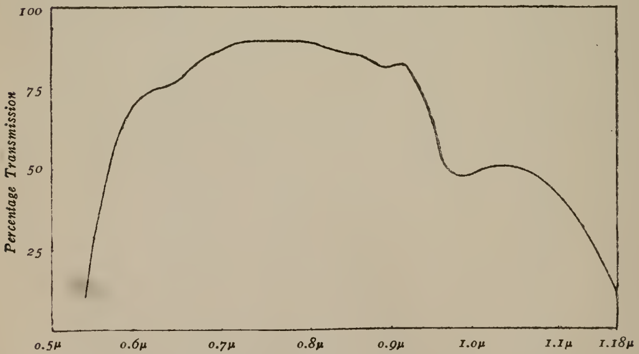

Fig. XXIII—Cobalt Bromide. Cell depth, 10 mm.; concentration, 0.347 N

a broad but slight absorption over the region near λ6500, and reach a maximum transmission over the region near λ7000 to λ8000. The curves then descend, showing a series

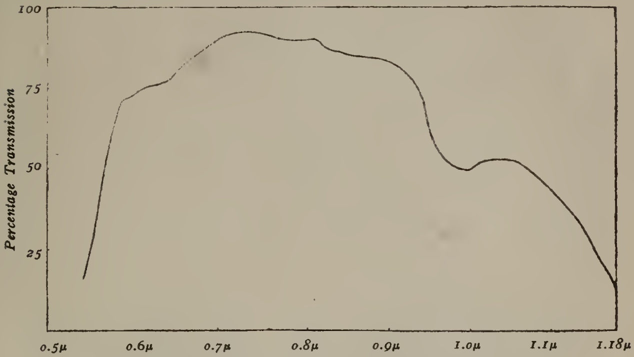

Fig. XXIV—Cobalt Nitrate. Cell depth, 10 mm.; concentration, 0.347 N

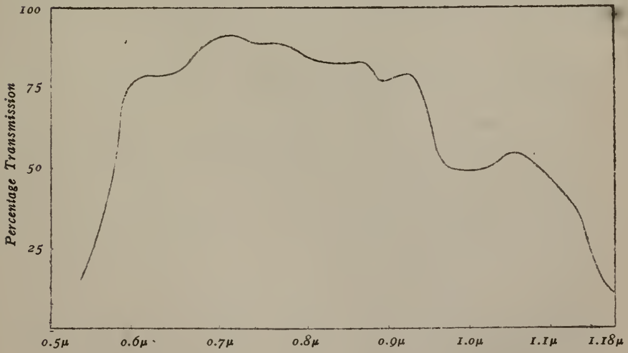

Fig. XXV—Cobalt Sulphate. Cell depth, 10 mm.; concentration, 0.347 N

of small absorption regions near λ8400, λ8900 and λ9800. The last of these absorption bands shows a fairly sharp edge towards the shorter wave lengths. Beyond λ10,500 the absorption increases rapidly until the region is reached where water is practically opaque.

Fig. XXV, representing the curve of transmission of cobalt sulphate, appears slightly different from the curves of the other salts of cobalt, having better defined bands in the region of λ8000.

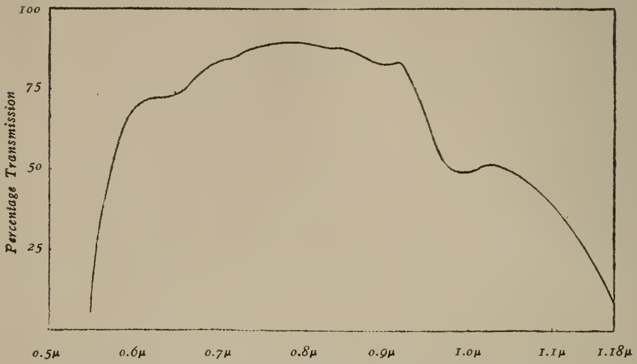

Fig. XXVI—Cobalt Acetate. Cell depth, 10 mm.; concentration, 0.347 N

GENERAL DISCUSSION OF THE RESULTS OBTAINED WITH THE RADIOMICROMETER

The introduction of the *radiomicrometer* into the work converted it into a quantitative study of the absorption spectra of solutions. The grating spectroscope and photographic method were very efficient in locating the positions of the absorption lines and bands from wave lengths λ2000 to about λ7600; and the photographic method gave some approximate idea as to the intensities of the various lines and bands. This method is, however, only roughly quantitative, and is very limited in the range of wave lengths to which it can be applied.

The radiomicrometer provides us with a quantitative method for studying the intensities of the various lines and bands, and also greatly extends the range of wave lengths that can be studied. In the earlier work with the radiomicrometer much time and labor were expended in perfecting the instrument, especially in constructing a sensitive radiomicrometer with a short period. Dr. Guy accomplished this very successfully.

The earlier work was practically limited to the study of the absorption spectra of solutions of neodymium salts—neodymium chloride, bromide, nitrate and acetate.

The results were plotted in what is known as transmission curves, which express the percentage transmission for the different wave lengths. Solutions of different concentrations of a given salt were studied, the depth of layer of the solution varying inversely as its concentration. The product of the depth of layer times the concentration is a constant. If the solvent plays no role in the absorption, then the transmission curves for the different concentrations of any given salts must fall directly over one another—the different curves would be the same curve.

We found that, in general, the more concentrated the solution the less the transparency and the broader the absorption bands; this is exactly what we obtained with the grating spectroscope and the photographic method. But in the more dilute solution the intensity of the bands was greater. We observed further that with increase in dilution the middle of the band is displaced towards the longer wave lengths.

The same general changes with dilution in the absorption spectra of solutions of neodymium bromide were observed as with the chloride; the more dilute the solution the narrower and more intense the bands.

The bands of neodymium nitrate, in general, show the same changes with dilution as those of the chloride and bromide. With increase in dilution the intensities of the bands increase, and their centers are displaced somewhat towards the longer wave lengths.

The three salts of neodymium, then, all show an increase in intensity with dilution. A possible explanation of this phenomenon, based upon resonance, has been offered. It is a well-known fact that a resonator, when excited by vibrations from a single vibrating resonator having the same pitch, vibrates more strongly than when set into vibration by a large number of resonators, one of which has the same pitch as its own and the others slightly different periods. In a word, if several vibrators are near together, every one exerts a certain influence on the others. The result is that no one of them has exactly the same period as the original resonator. Each resonator damps the other and we have less perfect resonance.

In a concentrated solution the resonators are relatively close together and mutually affect one another. The result is imperfect resonance, and the absorption bands are less intense in the more concentrated solution.

In the more dilute solution the vibrators are farther removed from one another and are surrounded by large amounts of water of hydration. The damping effect would thus be diminished. In such cases we would have more perfect resonance and the resulting absorption bands would be more intense.

Subsequent work has, however, shown that a part of this effect can possibly be explained as due to the fact that the slit width used was not infinitesimal.

It was found by the radiomicrometer, as with the grating spectroscope and photographic plate, that for a given concentration the acetate absorbs much more than any other salt of neodymium.

One of the most interesting facts thus far established by means of the radiomicrometer is the *effect of the dissolved substance on the absorption spectra of water*. We noted that aqueous solutions of hydrated salts were often more transparent than pure water. This is obviously a very remarkable fact, and we at once took up its careful study. We compared the absorption of aqueous solutions of strongly hydrated salts with the absorption of a layer of water equal in depth to the water in the solution through which the light was passed. We then carried out similar experiments with salts which, in the presence of water, combine with only a small amount of it. In a word, we compared the absorption of light by water with the absorption of an equal depth of water in aqueous solutions of strongly hydrated salts, and the absorption of light by water with an equal depth of water in aqueous solutions of salts which are scarcely hydrated at all.

The nonhydrated salts with which we worked were potassium chloride, ammonium chloride, and ammonium nitrate. It was necessary in all of this work to choose salts which themselves have little or no absorption in the region in which water absorbs, i. e., in the infrared. It was found that aqueous solutions of the above-mentioned compounds showed the same absorption of light as water having the same depth as the water in the solutions in question. This is exactly what would be expected. The dissolved substance and the solvent do not combine with one another to any appreciable extent, and it would be very difficult to see how either could appreciably affect the absorbing power of the other.

When we turn to the strongly hydrating salts, very different relations manifest themselves. The salts of this class that were studied were calcium chloride, magnesium chloride and aluminium sulphate.

In the case of a 5.3 normal solution of calcium chloride, the solution is the more transparent from 0.9 μ nearly to 1 μ. The water then becomes the more transparent for a short distance. From 1.05 μ to 1.2 μ the solution is the more transparent, becoming as much as 25 per cent. more transparent than the pure water. The water becomes more transparent than the solution only at and near the *bottom of the* "*water bands*" at approximately 1 μ. This is what we should expect if the solute exerts a damping effect on the absorbing power of water. When a smaller depth of the solution of calcium chloride is used, the water in the region 1.25 μ is more transparent than the solution. From this band on to the longer wave lengths the solution becomes more transparent than the water until 1.42 μ is reached, when both solution and water are practically opaque.

The results for magnesium chloride are essentially the same as those obtained for calcium chloride. The main difference is that from 1.0 μ to 1.1 μ, in the case of magnesium chloride, the water is more transparent; while for calcium chloride in this region the solution is the more transparent. The difference between water and the solution of magnesium chloride in this region is, however, not great. For longer wave lengths than 1.1 μ, the solution of magnesium chloride, like the solution of calcium chloride, is more transparent than the water, the difference for the two salts being of the same order of magnitude.

When a smaller depth of layer of the solution was used, the water was the more transparent from 1.22 μ to 1.34 μ. For the longer wave lengths the solution was the more transparent.

The curve for aluminium sulphate brings out this new feature: at 1 μ the solution is more transparent than the water. Beyond 1.04 μ the water is transparent to 1.17 μ, beyond which the solution is the more transparent, as with magnesium and calcium chlorides.

In the region of 1.2 μ water is the more opaque when a shallower layer of solution is used. From 1.29 μ to 1.36 μ, water is the more transparent; beyond 1.36 μ the solution is the more transparent.

The explanation of these remarkable results is that they must be due to some action of the dissolved substance on the solvent. That the solvent can affect the absorption spectra of the solution was first shown by Jones and Anderson;[1] and a large number of examples of this same action has since been found by Jones and Strong.[2] The action was satisfactorily explained as due to a combination of the solvent with the dissolved substance, and this explanation accounted for many facts which could not be otherwise satisfactorily explained. This theory of solvation in solution has aided us in explaining many phenomena which the theory of electrolytic dissociation alone could not account for, as has frequently been pointed out.

The same solvate theory of solution seems to aid us in explaining the facts just discussed. Those substances that do not form hydrates when in the presence of water show normal results as far as absorption spectra are concerned. Their solutions have the same absorption as so much pure water, the substance itself showing no absorption.

It is the hydrated salts, and only these, which give the abnormal results herein recorded. *The combined water seems to have less power to absorb light than free or uncombined water.* This would account for all of the facts observed.

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[1] Carnegie Institution, Washington, Publication 110.

[2] *Ibid.*, 130 and 160.

It should be noted that the presence of the salt shifts the absorption of the water towards the longer wave lengths. It was earlier observed that rise in temperature and increase in concentration shifted the absorption of the salt towards the longer wave lengths. The effect of rise in temperature and of increase in concentration is to simplify the hydrates existing in the solution. This simplified resonator shifts the absorption towards the red. The effect of the salt on the absorption of the water is the same as rise in temperature and increase in the concentration of the solution on the absorption of the dissolved substance. It may be that the dissolved substance diminishes the association of the solvent and thus simplifies the resonator. This may be true especially with the water of hydration or the water combined with the dissolved substance.

This new line of spectroscopic evidence bearing on the solvate theory of solution is regarded as probably the most direct that we have or can hope to obtain in favor of the view that there is combination between solvent and solute.

In studying the *absorption spectra of salts*, the intensity of the light after passing through the solution of the salt in question was compared with the intensity of the light after passing through a depth of water equal to the water in the solution in question.

The absorption spectrum of neodymium chloride shows three pronounced minima representing the three absorption bands with their centers near λ7300, λ7950 and λ8700, and less pronounced bands near λ7150 and λ9000. The latter may be due in part to the solvent; for all four dilutions studied the λ7300 and λ7900 bands show complete absorption over a considerable range of wave lengths. The minimum of band λ8700 is gradually lowered with increasing dilution.

The maximum transmission of solutions of neodymium chloride occur near λ7600 and λ8400, these solutions becoming almost completely transparent beyond 1 μ, except for the absorption of the solvent of this region. It seems that Beer's law holds, in general, for the infrared absorption of solutions of neodymium chloride.

The minima in the curves for the more dilute solutions of neodymium chloride are in about the same positions as those in the more concentrated solutions, but the solutions being more dilute are more transparent; hence the minima are not so pronounced. The maximal absorption occurs near λ7300 and λ7900. The λ8700 band has a minimum transmission of 64 per cent. There is complete transmission in the regions λ7200, λ7600, λ8300 and λ9300. The drop in all of the curves beyond 0.9μ is due to the absorption of the water.

With further increase in the dilution of the solution, there is a lowering of the maxima. The change is most pronounced in the λ8700 band, and here the absorption of the water is the most pronounced. The absorption of the water, together with the correction for its width, may account for this change, and Beer's law may hold for the dilute solutions of neodymium chloride almost as well as for the more concentrated.

Neodymium nitrate shows three minima at λ7300, λ7950 and λ8750. The nitrate bands are not as intense as those of the chloride, the solution of the nitrate not being as concentrated as that of the chloride. The nitrate bands, like those of the chloride, become more intense with increase in dilution. The absorption of water becomes more and more pronounced beyond 1μ.

The minima for solutions of neodymium acetate fall at approximately the same positions as with the chloride and nitrate.

Solutions of neodymium acetate, as indicated by the photographic method, show greater absorbing power than those of either the chloride or nitrate. The λ7000 band is slightly more intense in the acetate. The more intense bands, λ7300 and λ7950, show the same tendency to have their minima lowered with increasing dilution. There is a rapid increase in the absorption near λ9500, due to the water present in the solution.

Solutions of praseodymium salts are transparent in the infrared as far as 1.5μ, except two very weak bands which fall in the midst of the intense water bands. Praseodymium salts have two groups of bands, one in the green near λ4600 and another near λ5900. We have limited our investigations to the latter band, on account of the small amount of energy transmitted at λ4600. The curves representing the absorption of different concentrations of praseodymium chloride are identical to within the limits of possible experimental error. The results obtained with the radiomicrometer are in accord with those found by the grating and photographic plate. The minimum in each case occurs near λ5900. The total deviation from Beer's law, as shown by solutions of praseodymium chloride, is within the limits of experimental error.

The curves for praseodymium nitrate show that Beer's law holds here as well as for the chloride.

Solutions of nickel chloride show an increasing absorption from λ5200 to λ6300, where it is complete. Complete absorption extends to λ7200. Transmission increases to λ9000, then decreases to zero at λ10000. The visible spectrum of salts of nickel consists of intense broad absorption bands in the blue and red, having a single region of transmission in the red, extending to about λ6500. By means of the radiomicrometer we could study the region of transmission near λ9000. Beyond this we could not go because of the absorption of water.

The absorption of nickel nitrate closely resembles that of the chloride. There is maximal absorption at λ5400 and λ9000. There is complete absorption in the region λ7000 and beyond 1.1 μ.

The solution of nickel sulphate studied is slightly more dilute than the chloride and nitrate. In no region is there complete absorption. There is maximal transmission near λ5400 and λ9000, and minima at λ6900 and λ11000. Readings were not extended beyond this region on account of the intense absorption of water. The three salts of nickel studied have just about the same absorption spectra, the curves showing maxima and minima in just about the same regions of the spectrum.

Salts of cobalt in the visible region have a strong ultraviolet absorption. There is a band in the orange near λ5000, and increasing transmission towards the red. The infrared absorption of solutions of cobalt salts was studied, and the absorption of the chloride, bromide, nitrate, sulphate and acetate compared. The transmission curves for all of these salts have maxima at λ5950, λ7800, λ9100 and λ10600.

The transmission curves for all of the salts of cobalt studied rise rapidly from λ5000 to λ5900. The curves show a broad, slight absorption over the region near λ6500, and reach a maximum transmission from λ7000 to λ8000. There is a series of small absorption regions near λ8400, λ8900 and λ9800. Beyond λ10500 the absorption increases rapidly to the region where water is practically opaque.

The curves for cobalt sulphate are slightly better defined than those of the other cobalt salts.

In conclusion, we wish to express our thanks to Prof. A. H. Pfund for valuable suggestions, and to Dr. E. J. Shaeffer, who assisted in making the readings.

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DOUBLE CHLORIDES OF FERRIC AND FERROUS IRON WITH SOME AROMATIC BASES[1]

BY RAPHAEL MONROE MCKENZIE

Up to the time of beginning this work no double halides of iron and organic bases had been prepared and only a few such compounds containing metallic halides. In 1894 Walden[2] published the results of a systematic study of the double halides of ferric iron with rubidium, caesium, potassium and ammonium and found that they all conformed to Remsen's law,[3] as did all such compounds that had previously been described. In this investigation the double chlorides of ferric iron with aniline, *o*-, *m*- and *p*-toluidine, and of ferrous iron with aniline and with *o*-toluidine are described.

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[1] Abstract of a dissertation submitted to the Board of University Studies of the Johns Hopkins University in partial fulfilment of the requirements for the degree of Doctor of Philosophy. The work was completed a number of years ago and the results would have been published sooner but for the fact that it seemed desirable to repeat a part of it. This has been prevented and it seems best now to publish the results without further delay. The investigation is one of a series undertaken with the object of testing a generalization arrived at regarding the composition of the double halides (THIS JOURNAL, **11**, 291).—I. R.

[2] Am. J. Sci., [3] **48**, 283.

[3] THIS JOURNAL, **11**, 291.

Methods of Analysis

Purification.—To purify the salts for analysis they were filtered off with the aid of the pump, pressed between layers of filter paper to dryness, and the last of the hydrochloric acid extracted by letting them stand in a desiccator over sulphuric acid and solid potassium hydroxide. This method, slightly modified, was used by Neumann.[1] The analytical results were often not as close to the values required by the theory as could be desired, owing to the method of formation and of purification, and to the properties of the salts. They are all decomposed by water and can be recrystallized only from concentrated hydrochloric acid. Some of them are decomposed even by the concentrated acid, the hydrochlorides of the organic base separating alone from the solution on cooling.

Iron.—The weighed salt was dropped into a porcelain dish containing an excess of a weak solution of potassium hydroxide. The dish was then heated on a sand bath until the solution no longer gave any odor of aniline or of toluidine, water being added from time to time. An excess of hydrochloric acid was then added. As in many cases the organic base had caused some reduction, a small amount of hydrogen peroxide was added, and the solution was then evaporated to dryness. A little more acid was now added, and it was again evaporated to dryness. In the case of ferrous salts the oxidation with hydrogen peroxide was, of course, always required. The ferric chloride was then filtered into a pressure bottle through washed asbestos, to separate any precipitate formed by action on the aniline. The filtrate was then treated with a solution of potassium hydroxide until a slight permanent precipitate of ferric hydroxide separated; 0.2 cc. of dilute hydrochloric acid was added, and 1 gram of potassium iodide introduced. The bottle was then closed and heated at about 60° for twenty minutes. After cooling, the iodide set free was titrated in the bottle by use of starch and a solution of sodium thiosulphate, 1 cc. of which corresponds to 1 milligram of iron. The results were quite satisfactory.

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[1] Ann. Chem. (Liebig), **244**, 33.

The use of an open dish in place of a flask when boiling off the aniline or toluidine greatly lessened the time required. The use of the open dish and the evaporation of the ferric chloride to dryness were found necessary to ensure the complete removal of the hydrogen peroxide. The hydrogen peroxide is more stable than was formerly supposed.[1] It was found that hydrogen peroxide passed off with the steam and condensed on the side of a flask running back into the solution and causing error in analysis. The water which condensed on a watch glass held in the steam above the flask also gave a strong reaction for hydrogen peroxide when tested with iodized starch paper.

Chlorine.—A weighed sample of the salt was dropped into an Erlenmeyer flask containing a solution of pure potassium hydroxide, which was in excess of the amount required to decompose the salt. The alkaline solution was then boiled until the odor of aniline or toluidine was no longer noticed in the steam given off. Then the solution, formed on dissolving the ferric hydroxide in an excess of nitric acid, remained colorless. If all the organic base had not been driven off with the water vapor, a colored solution was formed. To the acid solution 5 cc. of a saturated solution of ferric ammonium alum was added, and the cold solution was titrated by Volhard's method in the flask.

In the case of the ferrous salts, a cold solution of the salt in very dilute nitric acid could be titrated directly without boiling off the organic base. But in most cases the method given above was used.

Water of Crystallization.—All attempts to make quantitative determinations of the water in these salts were unsuccessful. Samples of the salts, placed in the sulphuric acid desiccator, did not come to constant weights even after standing more than a month. It was found that the inside of the desiccator and the watch glass containing the salt became coated with a sublimate.

Samples of the salts were heated at 90°–110° in a glass tube, the closed end of which was placed in an air bath while the other end extended out into the air. Here it was found that a sublimate was deposited on the cool part of the tube. These trials showed that the water could not be determined by difference.

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[1] Ber. d. chem.Ges., **27**, 3307.

It was then thought that the water might be determined by absorption in a drying tube. To try this a sample of the salt was heated in a porcelain boat, within a glass tube which extended through an air bath. Air was drawn slowly through the tube while the air bath was heated to 100°, when it was found that the aniline hydrochloride and also the toluidine hydrochloride sublimed and were deposited on the cooler parts of the tube, while the water was carried farther to still colder portions of the tube. To determine whether water alone was carried on by the air current, a U-tube, containing a solution of silver nitrate, was attached to the front end of the tube and the air was drawn through it. After a few minutes the solution became cloudy and a precipitate formed, showing that compounds containing chlorine were carried over. This prevented further attempts being made to determine the water quantitatively.

The presence or absence of water was determined qualitatively, thus: The combustion tube was united to a drying tube, at the back, and to an empty, dry U-tube, and this to a drying tube, at the front. The U-tube was cooled by placing it in cold water. The salt was heated in the porcelain boat as before, and air was drawn through the system. If the salts contained water it was deposited on the walls of the U-tube as dew or in drops, the amount deposited giving some idea of the proportion of water in the salt and confirming the analytical results.

Some of the salts were analyzed before this method was used and in these cases nothing has been said as to the water, though the analytical results require the assumption that water was contained in them.

The atomic weights used in the calculations were: H, 1; O, 16; N, 14; Cl, 35.4; Fe, 56; C, 12.

Oxidation of Ferric Chloride

Much difficulty was experienced in the early part of the work, owing to the tendency of ferric chloride to oxidize the organic base. Thus, when a solution of ferric chloride and aniline hydrochloride was heated, the aniline was decomposed[1] and the ferric chloride reduced. In many cases a blue flocculent precipitate separated in such quantity as to fill the solution. In other cases it separated in smaller amounts, but interfered with obtaining pure salts. Slightly acid solutions were made in the ratio of one molecule of ferric chloride to two molecules of aniline hydrochloride, of one to four and of one to five. The first solution became light green on mixing and darkened on heating, when it became filled with the blue precipitate. The second solution with a smaller proportion of ferric chloride was lighter green than the first, but on heating and standing it darkened, and the precipitate formed. The third solution had a yellowish green color on mixing, but on heating, the upper layer, exposed to the air, became green; then the precipitate started to form and soon spread through the whole solution.

It was found later that the oxidizing action of the ferric chloride was greatest in slightly acid solution and that it was decreased by the addition of strong hydrochloric acid. Solutions made up by dissolving the aniline hydrochloride in a mixture of three parts concentrated hydrochloric acid to one part of water, and adding the ferric chloride, could be boiled with little or no formation of the precipitate.

In the work on *o*-toluidine hydrochloride it was found that the oxidizing action of the ferric chloride could not be prevented by increasing the amount of acid in the solution. Even solutions which had been saturated with hydrochloric acid gas decomposed on heating.

Ladenburg[2] describes the product formed by the action of ferric chloride on *o*-toluidine hydrochloride as the blue dye—toluidine blue—which separates as a flocculent precipitate. It is colored green by hydrochloric acid. The *p*-toluidine hydrochloride does not form such a compound. These results were confirmed in this work.

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[1] Jegel: Jahresb. chem. Technologie, **1875**, 955.

[2] Ber. d. chem.Ges., **1877**, 1127.

This behavior of *o*-toluidine hydrochloride led to some qualitative experiments as to the relative ease and rate of oxidation of aniline hydrochloride, and of *o*-, *m*- and *p*-toluidine hydrochlorides by ferric chloride.

These experiments showed that *o*-toluidine hydrochloride is the most readily acted on by the ferric chloride; *m*-toluidine hydrochloride comes next; aniline hydrochloride is less easily attacked, while *p*-toluidine hydrochloride is not acted on, as will also be seen later.

Dianiline Chloroferrate,

$FeCl_3.2C_6H_5NH_3Cl$

Solutions of ferric chloride and aniline hydrochloride in the ratios of 2 molecules of the former to one of the latter, of 3 : 1, of 4 : 1, and of 8 : 1, give this salt. The 2 : 1 and 3 : 1 solutions may give, first, the hexaniline chloroferrate, and then—on further concentration—a crop of this salt.

Solution in the Ratio of 2: 1.—A solution was made by adding 16 cc. of a solution of ferric chloride, containing 6 grams of ferric chloride, about 50 cc. of hydrochloric acid, i. e., nearly three parts of the concentrated acid to one part of water, and dissolving in it 2.4 grams of aniline hydrochloride. After evaporating for some time on the sand bath and cooling, no crystals separated. The solution was evaporated further and allowed to stand four days over sulphuric acid, when a crop of crystals separated as long, thick needles. These crystals in mass had a dark green color; the dry powder was a lighter green in color. This sample was analyzed. No water was given off on heating the salt.

Solution in the Ratio of 3 : 1.—A solution of this ratio gave on cooling a crop of the hexaniline chloroferrate. The mother liquor on standing over sulphuric acid for a week gave a crop of long, thick needles, which, after drying, appeared to be the same green salt that was obtained from the 2 : 1 solution. Not enough of the salt was obtained for analysis.

Solution in the Ratio of 4 : 1.—A solution was made by adding 2.4 grams of aniline hydrochloride to 32 cc. of a solution of ferric chloride, containing 12 grams of ferric chloride, and diluting slightly with hydrochloric acid. A green precipitate was formed which was filtered off through glass wool, and the solution was cooled, but no salt separated. After further concentration crystals separated on cooling as long plates 1–2 cm. in length. They had a resinous brown color; the dry powder was green. On standing over sulphuric acid a second crop of crystals, which looked black in solution, separated. On drying they were found to be long, thin, brownish green plates. There was also a crop of ferrous chloride.

The analysis of this second crop and of the salt from the 2 : 1 solution gave the following results:

	Calculated for $FeCl_3.2C_6H_5NH_3Cl$	Found Salt from Solution 4 : 1	 2 : 1
Chlorine	42.04	41.87	41.85
		42.07	42.95
Iron	13.30	13.06	...
		13.36	13.34

This salt seemed to change its crystalline form according to the conditions of formation. When it was obtained by cooling a hot concentrated solution the plates separated with the brown color. By slow evaporation of the solution over sulphuric acid, the salt was deposited in needles or prisms. The salt is very soluble in weak hydrochloric acid and in water. Some specimens also showed a tendency to take up water on standing.

Hydrous Dianiline Chloroferrate,

$FeCl_3.2C_6H_5NH_3Cl.H_2O$

A solution in the ratio of 4 : 1 was prepared by adding 18 cc. of concentrated hydrochloric acid to 32 cc. of a solution of ferric chloride, which contained 12 grams of ferric chloride, and dissolving in this 2.4 grams of aniline hydrochloride. From the solution, a crop of long, thin needles was obtained. In solution these looked black, but in dry condition they were green. Two and seven-tenths grams of the salt were obtained.

The results of the analysis are the following:

	Calculated for $FeCl_3.2C_6H_5NH_3Cl.H_2O$	Found
Chlorine	40.32	40.26
Iron	12.75	12.60

Hexaniline Chloroferrate,
$FeCl_3.6C_6H_5NH_3Cl$

The preliminary work on this salt was entirely unsuccessful, owing to the oxidation of the aniline hydrochloride, as above mentioned. The salt can be obtained only from strongly acid solutions. It is a beautifully crystalline salt of an orange color, though the color changes with the crystalline habit: and this is dependent on the conditions. This was seen, also, in the case of the dianiline chloroferrate. It is obtained from some solutions in yellow silky needles, either parallel or radiating from a point. By slow cooling or by evaporation over sulphuric acid, it is formed in prisms or heavy needles crystallizing in bunches, where the crystals cross each other in the middle, giving a very beautiful appearance.

The salt is very soluble in water, alcohol and dilute acids; but it is decomposed at the same time, since the ferric chloride oxidizes the aniline hydrochloride to form the blue precipitate previously described. The solutions of the salt in hydrochloric acid, of specific gravity about 1.12, range from light yellow in dilute solutions to blackish green in concentrated solutions, which have stood a short time. When the salt is dropped into a solution of sodium hydroxide, or better when such a solution is added to a solution of the salt in dilute hydrochloric acid, the aniline collects in drops on the surface, and the iron is precipitated as red ferric hydroxide. The dianiline chloroferrate acts similarly and the solutions of both salts give all the tests for ferric iron.

This salt was obtained from solutions of ferric chloride and aniline hydrochloride in all the ratios of 3 : 1, 2 : 1, 1 : 1, 1 : 2, 1 : 3, 1 : 4 and 1 : 8. In the 3 : 1 and 2 : 1 solutions either this or the dianiline chloroferrate may separate; or first, a crop of the hexaniline chloroferrate may separate and then, from the mother liquor, a crop of the dianiline salt may be deposited, as above described.

Solution in the Ratio of 3 : 1.—Twenty-four cc. of a solution of ferric chloride, containing 9 grams of ferric chloride, was diluted with 10 cc. of concentrated hydrochloric acid, and in it was dissolved 2.4 grams of aniline hydrochloride. The solution, on standing, deposited a bunch of long, yellow needles.

Another solution in the ratio of 3 : 1 was made, which contained 6 grams of ferric chloride and 1.6 grams of aniline hydrochloride. A crop of yellow, fine, silky needles was deposited fron the solution.

Both of these salts were analyzed with the following results:

	Calculated for $FeCl_3.6C_6H_5NH_3Cl$	Found	
		First preparation	Second preparation
Chlorine	33·94	34·38	35·27
Iron	5·96	6.47	6.48

Solution in the Ratio of 2 : 1.—Sixteen cc. of a solution of ferric chloride, containing 6 grams of ferric chloride, was added to 18 cc. of concentrated hydrochloric acid, and in this was dissolved 2.4 grams of aniline hydrochloride. On cooling this solution, a crop of fine, silky crystals of a brownish yellow color separated. One and five-tenths grams of the salt were obtained.

Solution in the Ratio of 1 : 1.—A solution was made by mixing 16 cc. of a solution of ferric chloride, containing 6 grams of ferric chloride, with 18 cc. of concentrated hydrochloric acid and adding 4.8 grams of aniline hydrochloride. From this solution 3.1 grams of a salt was obtained in the form of fine, silky needles, which in the solution had a golden yellow color. The results of the analyses of these salts were the following:

	Calculated for $FeCl_3.6C_6H_6NH_3Cl$	Found for salt from	
		Solution 2 : 1	Solution 1 :1
Chlorine	33·94	33·44	33·48
Iron	5·96	6.38	6.10

No water was given off on heating the salt from the 2 : 1 solution; the salt from the 1 : 1 solution was not tested.

Solution in the Ratio of 1 : 2.—A solution of 16 cc. of ferric chloride, equal to 6 grams of ferric chloride, was added to 20 cc. of concentrated hydrochloric acid, and 9.6 grams of aniline hydrochloride was dissolved in it. It was difficult to dissolve all the aniline hydrochloride; so the solution was further diluted to keep all the double salt dissolved. Six and forty-seven hundredths grams of the salt separated, on cooling, in larger needles than those obtained from the preceding solutions. They were also of a darker yellow color when in the solution, and when dried they had a brownish tint.

Solution in the Ratio of 1 : 4.—A solution containing 3 grams of ferric chloride and 9.5 grams of aniline hydrochloride was made up with hydrochloric acid to a volume of 50 cc. On cooling the salt separated in yellow needles. The analyses of these salts gave the following results:

	Calculated for	Found for salt from	
	$FeCl_3.6C_6H_5NH_3Cl$	Solution 1 : 2	Solution 1 : 4
Chlorine	33·94	34·64	33·45
			33·50
Iron	5·96	5.61	6.03
			6.19

The salt was best obtained from a solution in the ratio of 1 : 4 as follows: Eleven and six-tenths cc. of a solution of ferric chloride, containing 3 grams of ferric chloride, was diluted to 75 cc. with hydrochloric acid—three parts of concentrated acid to one part water—and in it was dissolved 9.4 grams of aniline hydrochloride. The solution was heated on a water bath, when it turned a deep brownish red and remained perfectly clear. The salt crystallized in needles and prisms, which had a yellow color when viewed on the side, but when viewed on the ends they showed a decided red color. The dry salt in coarse powder had a reddish yellow color, but in fine powder it was a pure yellow. Six grams of the crystals were obtained.

Another preparation of the salt was made just as above. Part of the salt was dried and prepared for analysis; a second part was recrystallized from concentrated hydrochloric acid. The recrystallized salt formed, like that from the first 1 : 4 solution, in needles crossing each other in the middle. The mother liquor from this specimen, on standing over sulphuric acid, gave a crop of single needles starting at the surface of the liquid and extending down through the solution.

The three portions gave these results on analysis:

	Calculated for $FeCl_3.6C_6H_5NH_3Cl$	Found Uncrystallized	Found Recrystallized 1st crop	Found Recrystallized 2nd crop
Chlorine	33·94	33·39		
		33·80	33·76	33·83
Iron	5·96	6.09	6.12	
		6.29		
Nitrogen	8.95	8.41		
		8.45		
		No water given off on heating		No water given off on heating

Solution in the Ratio of 1 : 8.—A solution was prepared containing 3 grams of ferric chloride and 19.1 grams of aniline hydrochloride. The salt prepared in yellow crystals as fine needles and in prisms which frayed off on the ends into long, fine needles. These prisms cross in the middle.

The results of the analyses were the following:

	Calculated for $FeCl_3.6C_6H_6NH_3Cl$	Found
Chlorine	33·94	33·64
		33·78
Iron	5·96	5·94
		5·90

The salt gave off no water on heating to 100°.

Very fine specimens of the hexaniline chloroferrate were obtained from solutions of ferrous chloride and aniline hydrochloride during the work on the salts formed by the action of ferrous chloride on aniline hydrochloride. On exposure to the air the ferrous chloride became oxidized to ferric chloride which in the presence of excess of aniline hydrochloride formed the higher salt. In one case a specimen of the *dianiline* chloroferrate was obtained. The addition of a little hydrogen peroxide to the solution of the ferrous compounds also produced the hexaniline chloroferrate.

The crystalline form of the salt obtained thus was the same as when obtained from ferric chloride directly.

Analyses of some samples obtained thus gave the following results:

	Calculated for $FeCl_3.6C_6H_5NH_3Cl$	Found I	Found II	Found III
Chlorine	33.94	33.83 33.68	33.44 33.44	33.60 33.50
Iron	5.96	6.49	6.19 6.23	6.66 6.46

Hydrous Hexaniline Chloroferrate

$$FeCl_3.6C_6H_5NH_3Cl.2H_2O$$

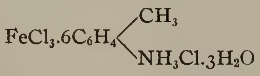
A solution of ferrous chloride and aniline hydrochloride in the ratio 2 : 1 had stood in contact with the air until it contained a large quantity of the orange *ferric* salt, the hexaniline chloroferrate. This was filtered off and recrystallized from concentrated hydrochloric acid.

On analysis it gave the following results:

	Calculated for $FeCl_3.6C_6H_5NH_3Cl.2H_2O$	Found
Iron	32.70	32.73 32.80
Chlorine	5.74	5.78 5.82

A second crop from the mother liquor gave analyses for the anhydrous salt. The results are given under the hexaniline chloroferrates, from ferrous chloride and aniline hydrochloride, No. I. An attempt was made to obtain the hydrous salt by recrystallizing the hexaniline chloroferrate, obtained from a solution of ferric chloride and aniline hydrochloride, from concentrated hydrochloric acid, but the *anhydrous* salt was obtained.

*Hexa-*o*-toluidine Chloroferrate,*



$$FeCl_3.6C_6H_4\left\langle\begin{matrix}CH_3\\NH_3Cl.3H_2O\end{matrix}\right.$$

The first attempts to obtain double salts with ferric chloride and *o*-toluidine hydrochloride were not satisfactory, owing to the easy oxidation of the toluidine hydrochloride by the ferric chloride.

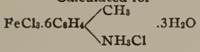
A solution of ferric chloride and *o*-toluidine hydrochloride in hydrochloric acid, part dilute acid and part concentrated acid, was made in the ratio of 1 : 1. It was heated to boiling, when a dark tarry oil separated. The solution was evaporated to about one-half and cooled, when a crystalline substance separated. The mother liquor, on standing over sulphuric acid, gave a crop of crystals in the form of needles having a brownish yellow color, and arranged in clusters.

Another solution in the ratio of 1 : 1, and a solution in the ratio of 2 : 1 were prepared. From these, however, only a slight amount of the double salt was obtained, mixed with tarry decomposition products. Ferrous chloride was also deposited. Most of the action in both solutions was the oxidation of the *o*-toluidine hydrochloride.

A solution nearly in the ratio of 1 : 1 was made from 17 cc. of a solution of ferric chloride, containing 6.4 grams ferric chloride, and 5.27 grams of *o*-toluidine hydrochloride in 34 cc. of dilute hydrochloric acid and 10 cc. of the concentrated acid. The solution, on heating, became first deep red, then quite black, and began to decompose. It was boiled about two hours, filtered and cooled; after a time, a crop of a salt separated. The salt formed a bunch of needles, which started to crystallize at a point on the side of the beaker and nearly filled the solution. Three and forty-seven hundredths grams of the reddish yellow salt were obtained.

Another solution in the ratio of 1 : 1, containing 6 grams of ferric chloride and 5.27 grams of *o*-toluidine hydrochloride, were made up with 10 cc. of dilute acid and 5 cc. of the concentrated acid. The solution was heated to boiling for about half an hour, when there was a slight oxidation of the *o*-toluidine hydrochloride. After filtering the hot solution and letting it cool, the salt filled the solution so that the beaker could be turned upside down without spilling the liquid. Four and forty-two hundredths grams of the salt were obtained. On drying between filter paper in the press the edges of these two samples turned green.

Analyses of the samples give the following results:

	Calculated for  $FeCl_3.6C_6H_4\langle^{CH_3}_{NH_3Cl}.3H_2O$	Found		
		1st sample	2nd sample	3rd sample
Chlorine	29.59	29.24	30.29	29.12 29.22
Iron	5.20	5.20	5.02 5.34	5.04 5.18

In other solutions in different ratios there was not so much success in the work; more of the oxidation product was formed.

New Method of Preparation.—It was thought that the double salt might be obtained from solutions of ferric chloride and *o*-toluidine hydrochloride dissolved in dilute hydrochloric acid of specific gravity 1.12, by saturating the solution with hydrochloric acid gas. This was tried with such success that it was used in all the subsequent work.

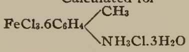
By this method the hexa-*o*-toluidine chloroferrate was obtained from solutions of ferric chloride and *o*-toluidine hydrochloride in ratios of 4 : 1, 2 : 1, 1 : 1, 1 : 4, 1 : 8 and 1 : 12. The salt could be recrystallized from concentrated hydrochloric acid by saturating the warm acid with the salt, and allowing the solution to cool; or by nearly saturating weak, cold hydrochloric acid with the salt and passing into the solution hydrochloric acid gas nearly to saturation. On trying to crystallize the salt from dilute acid it was decomposed and toluidine hydrochloride separated. In solution in water and in ethyl alcohol the salt decomposed into its constituents, which then reacted to form the oxidation product. Ethyl ether decomposed the salt, leaving a white solid. The crystals of the salt formed in best shape by slow evaporation of the strong hydrochloric acid solution over sulphuric acid and solid potassium hydroxide.

Solution in the Ratio of 4 : 1.—To 21 cc. of a solution of ferric chloride, containing 8 grams of ferric chloride, 1.77 grams of *o*-toluidine hydrochloride was added. The solution was prepared cold and allowed to stand about an hour and a half, during which time—the solution not being strongly acid—the substances had reacted so that the solution became green. This shows the ease with which ferric chloride acts on *o*-toluidine hydrochloride. The beaker containing the solution was placed in cold water while hydrochloric acid gas was passed into it. After filtering the solution it was allowed to stand overnight, when a crop of the salt separated in reddish yellow needles crystallizing in bunches.

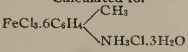
Solution in the Ratio of 2 : 1.—Thirty-two cc. of a solution of ferric chloride, containing 12 grams of ferric chloride and 5.27 grams of *o*-toluidine hydrochloride, gave a deposit of an amorphous powder when the cold solution was saturated with hydrochloric acid gas. This powder was filtered off and recrystallized by dissolving in hydrochloric acid—one-half concentrated acid to one-half dilute acid—and saturating the solution with hydrochloric acid gas. After standing four days over sulphuric acid, 2.5 grams of the needles were obtained.

Solution in the Ratio of 1 : 1.—To 16 cc. of a solution of ferric chloride, containing 6 grams of ferric chloride, 5.27 grams of *o*-toluidine hydrochloride were added, which did not all dissolve. The solution was nearly saturated with the hydrochloric acid gas. It became heated on absorbing the gas so that on cooling the salt separated in good condition.

The results of the analyses of these salts were the following:

	Calculated for	Found for salt from		
	 $FeCl_3.6C_6H_4\begin{cases}CH_3\\NH_3Cl.3H_2O\end{cases}$	Sol. 4 : 1	Sol. 2 : 1	Sol. 1 : 1
Chlorine	29.59	29.69	29.33	29.41
		29.69	29.31	29.43
Iron	5.20	5.76	5.42	5.83
		5.47	5.19	....

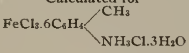
Solution in the Ratio of 1 : 4.—To 20 cc. of hydrochloric acid—1 part dilute acid to 1 part concentrated acid—1 gram of ferric chloride and 3.536 grams of *o*-toluidine hydrochloride were added. On saturating with hydrochloric acid gas the solution became nearly solid with the salt which separated. The salt was filtered off and as much of the liquid as possible was separated by use of the filter pump. The salt was divided into three parts: Part I was prepared for analysis without recrystallization; Part II was recrystallized by saturating hot concentrated acid with the salt and cooling; Part III was recrystallized by dissolving in the dilute acid and saturating the solution with the gas. There was not enough of the salt, from Part II, for the determination of both iron and chlorine. The results of the analyses are as follows:

	Calculated for	Found		
	 $FeCl_3.6C_6H_4\begin{smallmatrix}CH_3\\ NH_3Cl.3H_2O\end{smallmatrix}$	Part I	Part II	Part III
Chlorine	29.59	29.52	29.49	29.76
Iron	5.20	5.12	...	5.64

Solution in the Ratio of 1 : 8.—Two and seven-tenths cc. of a solution of ferric chloride—containing 1 gram of ferric chloride—was diluted to about 35 cc. with hydrochloric acid and 7.07 grams of *o*-toluidine hydrochloride were added. On saturating with hydrochloric acid gas the solution became nearly solid from the separation of the salt. About two-thirds of this solid mass was heated to 40° with 75 cc. of concentrated hydrochloric acid; on cooling *o*-toluidine hydrochloride separated. This was filtered off and from the filtrate the reddish yellow needles were obtained.

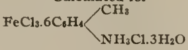
Solution in the Ratio of 1 : 12.—One gram of ferric chloride in solution and 10.609 grams of *o*-toluidine hydrochloride were dissolved in 40 cc. of concentrated hydrochloric acid. The solution was cooled and hydrochloric acid gas passed in, when on standing overnight both *o*-toluidine hydrochloride and the double salt crystallized out. By fractional crystallization the double salt was obtained pure.

The analyses of these samples gave these results:

	Calculated for	Found for salt from	
	 $FeCl_3.6C_6H_4\begin{smallmatrix}CH_3\\ NH_3Cl.3H_2O\end{smallmatrix}$	Sol. 1 : 8	Sol. 1 : 12
Chlorine	29.59	29.60	29.69
Iron	5.20	5.65	...

A sample of the salt from the 1 : 8 solution was heated at 95°–100°, when it gave off water. When heated to 125° it was found that *o*-toluidine hydrochloride had sublimed.

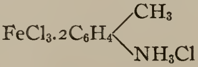
The hexa-*o*-toluidine chloroferrate was obtained also by oxidation of solutions of ferrous chloride and *o*-toluidine hydrochloride on exposure to the air. When it was attempted to obtain second crops of crystals from solutions of the ferrous chloride and toluidine hydrochloride the *ferric* double salt separated. Two samples of second crops of crystals from solutions of ferrous chloride and *o*-toluidine hydrochloride in the ratios 2 : 1 and 3 : 1 gave, on analysis, the following results:

	Calculated for  $FeCl_3.6C_6H_4\!<\!\begin{matrix}CH_3\\NH_3Cl.3H_2O\end{matrix}$	Found for salt from	
		Sol. 2 : 1	Sol. 3 : 1
Chlorine	29.59	29.25	29.36
Iron	5.20	5.95	5.35

Many attempts were made to prepare double chlorides of ferric chloride and *o*-toluidine hydrochloride containing a larger proportion of ferric chloride, but without success. Solutions in the ratio of 8 molecules of ferric chloride to 1 molecule of *o*-toluidine hydrochloride were made from 21 cc. of a solution of ferric chloride—containing 8 grams of ferric chloride—and 0.884 gram of dry *o*-toluidine hydrochloride. When these solutions were saturated in the cold, with gaseous hydrochloric acid, a little of a salt that seemed to be hexa-*o*-toluidine, chloroferrate, separated, but quickly dissolved. No salt could then be obtained from the solution even on cooling in ice water. On heating the solutions in order to concentrate them, the *o*-toluidine hydrochloride was destroyed, no matter how acid the solution had been made.

Attempts were also made to obtain a salt from a very nearly saturated solution of ferric chloride containing 8 grams of ferric chloride, to which was added 0.884 gram of *o*-toluidine hydrochloride, by saturating with the gaseous acid, and cooling in ice water, but without success.

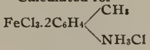
Di-m-*toluidine Chloroferrate,*



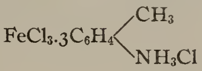
$$FeCl_3.2C_6H_4\!<\!\begin{matrix}CH_3\\NH_3Cl\end{matrix}$$

This salt separated from concentrated solutions of ferric chloride and *m*-toluidine hydrochloride in the ratio of four molecules of ferric chloride to one molecule of *m*-toluidine hydrochloride, 3 : 1, 2 : 1, 1 : 4 and 1 : 6, in shining, yellow plates when gaseous hydrochloric acid was passed into the solution.

The salt was deliquescent and could not readily be obtained in condition for analysis.

	Calculated for  $\mathrm{FeCl_3.2C_6H_4}\left\langle\begin{matrix}\mathrm{CH_3}\\ \mathrm{NH_3Cl}\end{matrix}\right.$	Found for salt from		
		Sol. 1 : 1	Sol. 1 : 4	Sol. 4 : 1
Chlorine	39.42	38.75	38.74	38.40
Iron	12.47	12.31	12.46	12.90

*Tri-*m*-toluidine Chloroferrate,*



$$\mathrm{FeCl_3.3C_6H_4}\left\langle\begin{matrix}\mathrm{CH_3}\\ \mathrm{NH_3Cl}\end{matrix}\right.$$

This salt could not be obtained in very satisfactory condition; only one specimen was obtained pure enough for analysis. When solutions in the ratios 1 : 3, 1 : 4 and 1 : 6 were saturated with hydrochloric acid gas, first the lower salt separated; but, on continued action of the acid, the lower salt changed its crystalline form and the higher salt was produced.

Solution in the Ratio of 1 : 3.—To a solution of 2.643 grams of *m*-toluidine hydrochloride in 6.2 cc. of dilute hydrochloric acid was added 3.88 cc. of a solution of ferric chloride containing 1 gram of ferric chloride. The beaker containing the solution was placed in cold water and hydrochloric acid gas was passed into it. When the oil separated the beaker was placed in crushed ice while the saturation with the gaseous acid continued. The solution cleared up and then crystals separated in two forms; all through the solution were yellow plates as in the 1 : 4 solution, then there were bunches of green crystals. These were all broken up with the stirring rod and 2.5 cc. of dilute hydrochloric acid were added. On continued absorption of hydrochloric acid gas the crystals changed form and the yellow plates were replaced by finer crystals of a lighter yellow color. When the change seemed to be complete, the mass—which looked like hexa-*o*-toluidine chloroferrate as it separated from concentrated solution—was filtered off.

The salt formed a sticky mass fuming with hydrochloric acid. It was very difficult to prepare for analysis, being deliquescent and adhering to the drying paper. The salt which was left, part of it having been dissolved by the moisture of the air and absorbed by the drying paper, was further dried in a desiccator.

Part of the salt before the final drying was dissolved in hot, concentrated hydrochloric acid and the solution was cooled in ice water. The salt which separated was the di-*m*-toluidine chloroferrate.

The analysis of the dried salt gave the following results:

Chlorine	35.61
Iron	10.17

The ratio of the iron to the chlorine in the salt was 1 : 5.54. Taking the ratio as 1 : 6 the salt must have been the tri-*m*-toluidine chloroferrate, for which the calculated percentages are: Chlorine, 35.85; iron, 9.45.

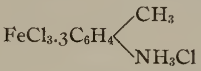
A second solution in the ratio of 1 : 3 was prepared which contained the same amounts of toluidine hydrochloride and of ferric chloride, but whose volume was 15 cc. This gave first the di-*m*-toluidine chloroferrate. The continued action of the hydrochloric acid gas produced the same change as before, but the substance which separated seemed to be a mixture of the two salts.

The ratio of the constituents was changed to 1 : 6 by the addition of 2.643 grams of the toluidine hydrochloride in 9 cc. of hydrochloric acid. The solution was warmed to bring all the salts into solution. When it had been cooled and hydrochloric acid gas passed into it, the di-*m*-toluidine chloroferrate separated without the formation of the oil. This salt did not change over to the higher salt so far as could be seen. When the beaker was removed from the ice water most of the salt was dissolved.

A second solution in ratio of 1 : 6 was prepared containing 0.5 gram of ferric chloride and 2.643 grams of *m*-toluidine hydrochloride in 10 cc. of liquid. The di-*m*-toluidine salt separated first, then some of the lighter fine crystals appeared, which seemed to be composed of fine needles. After one to two hours all the crystals seemed to have changed over to this form.

All attempts to get this crop of crystals in condition for analysis failed. The mother liquor could not be entirely separated by the use of the filter pump, and the solution was so strongly acid that the drying paper was disintegrated and mixed with the salt, so that they could not be separated. No further attempts to prepare this salt were made.

*Tri-*p*-toluidine Chloroferrate,*



$$\mathrm{FeCl_3.3C_6H_4}\left\langle\begin{matrix}\mathrm{CH_3}\\ \mathrm{NH_3Cl}\end{matrix}\right.$$

The first part of the work with ferric chloride and *p*-toluidine hydrochloride was very unsatisfactory. Solutions were made in the ratio of 1 : 1 and 1 : 4. From solutions in the ratio 1 : 4 only *p*-toluidine hydrochloride separated. From the solutions in the ratio 1 : 1 a salt was obtained in good shape; but on standing over sulphuric acid this broke down into its constituents.

It was thought from some previous work on ferrous chloride with *o*-toluidine hydrochloride that the union of the two chlorides might be facilitated by keeping the solution at the boiling temperature for a long time, but the preliminary work showed that this did not hold for ferric chloride and *p*-toluidine hydrochloride. This showed, also, that the double salt cannot exist except in strongly acid solution, and that the ferric chloride acts on *p*-toluidine hydrochloride much less than it does on *o*- and on *m*-toluidine hydrochloride.

Tri-*p*-toluidine chloroferrate was obtained from solutions of ferric chloride and *p*-toluidine hydrochloride in ratios of 2 molecules of ferric chloride to 1 of *p*-toluidine hydrochloride, of 3 : 1 and of 6 : 1. The salt separated from the solutions in lustrous red crystals whose form varied somewhat with the conditions of its preparation. In some cases it was obtained as plates, in other cases as thick prisms.

Solution in the Ratio of 2 : 1.—To 0.881 gram of *p*-toluidine hydrochloride dissolved in 15 cc. of dilute hydrochloric acid were added 3.1 cc. of a solution of ferric chloride, containing 2 grams of ferric chloride. The warm solution was treated with hydrochloric acid gas, when *p*-toluidine hydrochloride separated. It was then placed in ice water and the gas passed through the solution, but the salt did not separate. Thinking that the temperature might be too low, the solution was heated and the gaseous acid was passed in while the solution cooled. A double salt separated, but *p*-toluidine hydrochloride was mixed with it. From the mother liquor a double salt separated in short prisms with lustrous faces. As they were free from *p*-toluidine hydrochloride they were prepared for analysis.

Solution in the Ratio of 3 : 1.—A solution was prepared containing 6 grams of ferric chloride and 1.76 grams of *p*-toluidine hydrochloride in 40 cc. of dilute hydrochloric acid. The solution was heated to boiling and the hot, nearly opaque, red solution was treated with hydrochloric acid gas until it was strongly acid. It was then cooled and more of the gas passed into it. The absorption of the gas produced much heat. At first *p*-toluidine hydrochloride separated; this was then changed to the double salt. The salt was filtered off, when it was seen to be composed of reddish yellow plates. In fine powder the salt was of a darker color than were some of the specimens previously obtained.

The analyses of these salts gave the following results:

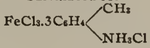
	Calculated for $FeCl_3.3C_6H_4\langle^{CH_3}_{NH_3Cl}$	Found for salt from	
		Sol. 2 : 1	Sol. 3 : 1
Chlorine	35.85	35.55	35.60
Iron	9.45	9.27	9.43
Nitrogen	7.04	....	6.80
Water	0.0	....	0.0

The salt from the 3 : 1 solution when heated at 110°–115° gave off no water, but a sublimate of toluidine hydrochloride was formed.

Solutions in the Ratio of 6 : 1.—To 9.3 cc. of a solution of ferric chloride, containing 6 grams of ferric chloride, was added 0.881 gram of *p*-toluidine hydrochloride. The solution was warmed slightly and hydrochloric acid gas was passed into it, when it became hot. The beaker was then placed in cold water while the saturation with the hydrochloric acid gas was continued. The solution was left overnight, when a crop of the red salt separated. This was prepared for analysis.

A second solution was made up like the last except that it was diluted with 10 cc. of dilute hydrochloric acid. The solution was saturated with hydrochloric acid gas as it cooled to near 0° in ice water, when a crop of the salt separated.

The results of the analyses of these samples of the salt were the following:

	Calculated for	Found for salt from	
	 $FeCl_3.3C_6H_4\left\langle {}^{CH_3}_{NH_3Cl} \right.$	First sol.	Second sol.
Chlorine	35.85	35.64	36.16
Iron	9.45	9.36	10.01

Salts from Ferrous Chloride and the Hydrochlorides of Aniline and o-*Toluidine*

Solutions of ferrous chloride and aniline hydrochloride in the ratios of 3 : 1, 2 : 1, 1 : 1, 1 : 2, in slightly acid solutions, gave mixtures of aniline hydrochloride in plates, nearly white or light yellow crystals in short needles, and, often mixed with these, red crystals in thicker, longer needles than the yellow ones. Then it was found that the solutions which were filtered hot in contact with the air or which stood for a long time exposed to the air gave a larger proportion of the red crystals. A sample of these, which was obtained free from the light yellow needles, gave the ordinary reactions of iron in the *ferric* state. The salt was analyzed and it proved to be hexaniline *chloroferrate*.

	Calculated for $FeCl_3.6C_6H_5NH_3Cl$	Found
Chlorine	33.94	33.53
Iron	5.96	6.80

The light yellow needles, when freshly prepared and quickly freed from the mother liquor, were nearly white, but they became slightly yellow before they could be filtered in quantity from the mother liquor. They gave all the reactions for iron in the ferrous state. The best test was the formation of the ferrous hydroxide and its instantaneous change to the red ferric hydroxide when hydrogen peroxide was added.

It was also found that a slightly acid solution of the ferrous chloride and aniline hydrochloride, which had deposited the aniline hydrochloride, gave a good yield of the light yellow needles when concentrated hydrochloric acid was poured into the solution. The change of the plates of aniline hydrochloride over to the needles of the double salt wherever the strong acid came in contact with them was very interesting to watch. It was then found that by using quite strongly acid solutions the ferrous double salt could be obtained, on the first cooling of the solution, free from the ferric salt. A sample of the light yellow crystals on analysis gave results that pointed to the formula $FeCl_2.2C_6H_5NH_3Cl.2H_2O$ for the salt.

	Calculated for $FeCl_2.2C_6H_5NH_3Cl.2H_2O$	Found
Chlorine	33.58	33.23
		32.89
Iron	13.28	14.44
		15.03

Dianiline Chloroferrite,
$FeCl_2.2C_6H_5NH_3Cl.2H_2O$

The salt was obtained from solutions containing all proportions of ferrous chloride and aniline hydrochloride, from 1 : 4 to such a ratio that ferrous chloride separated from the solution mixed with the double salt. In a series of experiments four solutions were made up in the ratios 4 : 1, 3 : 1, 2 : 1 and 1 : 1.

Solution in the Ratio of 4 : 1.—This solution contained 8.72 grams of ferrous chloride and 2.22 grams of aniline hydrochloride in 50 cc. of liquid. It was heated to boiling for a time, but on cooling no salt separated. When it was placed in snow a crop of the light yellow needles separated. By the next morning a second crop of the salt had formed at the ordinary temperature. The salt was filtered off and prepared for analysis.

Solution in the Ratio of 3 : 1.—This solution contained 6.54 grams of ferrous chloride and 2.22 grams of aniline hydrochloride in 39 cc. of liquid. The solution was boiled a short time and then cooled, when the light yellow salt separated at ordinary temperatures. This was filtered off and prepared for analysis. The next morning a second crop of the salt had formed, but it was mixed with crystals of ferrous chloride.

Solution in the Ratio of 2 : 1.—This solution was composed of 4.36 grams of ferrous chloride and 2.22 grams of aniline hydrochloride in 29 cc. of liquid. After boiling and cooling, the solution deposited about twice as much of the light yellow crystals as did the 3 : 1 solution. This crop of the salt was prepared for analysis. The second crop of the salt in this case also contained crystals of the ferrous chloride.

Solution in the Ratio of 1 : 1.—The solution contained 2.18 grams of ferrous chloride and 2.22 grams of aniline hydrochloride in 19 cc. of liquid. The solution was boiled and then allowed to cool, when it became nearly solid with the salt which had separated. The salt was dissolved by the addition of dilute hydrochloric acid and heating; it was then left overnight, when there was a crop of the light yellow crystals mixed with some of the red ferric salt. These were separated mechanically and the ferrous salt was prepared for analysis. The analyses of these crops gave the following results:

	Calculated for		Found for salt from		
	$FeCl_2.2C_6H_5NH_3Cl.2H_2O$	Sol. 4 : 1	Sol. 3 : 1.	Sol. 2 : 1	Sol. 1 : 1
Chlorine	33.58	33.75	33.91	33.61	33.66
		33.86	33.76	33.15	
Iron	13.28	14.12	13.31	14.16	...
			13.86	14.26	

The solution was made in the ratio of 1 : 2.5, which contained 13.68 grams of ferrous chloride and 32.9 grams of aniline hydrochloride in 183 cc. of solution. The solution was only slightly acid, so that on boiling and cooling only aniline hydrochloride separated. About one-half the volume of concentrated hydrochloric acid was added; the solution was then heated and allowed to cool, when the light yellow ferrous salt separated in large quantity. This was filtered off and prepared for analysis, the results of which were as follows:

	Calculated for $FeCl_2.2C_6H_5NH_3Cl.2H_2O$	Found
Chlorine	33.58	33.88
Iron	13.28	13.25

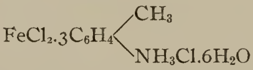
From the mother liquor more of the salt crystallized. This was left in the solution, when after two days the ferric salt appeared all through the mass. After standing some weeks the change to the ferric double salt seemed to be complete. This salt gave on analysis results agreeing with those required for the hexaniline chloroferrate.

The dianiline chloroferrite when heated in the air bath at 90° turned nearly black, and when this residue was dissolved in water a dark solution was obtained with some insoluble substance; the salt is therefore decomposed on heating even at 90°.

When allowed to stand in the sulphuric acid desiccator the salt loses weight, but, as before stated, in treating of the methods of analysis, the percentage of water could not be determined.

After remaining in the specimen tube a short time—a few weeks—these ferrous salts become green and show other signs of decomposition.

Tri-o-*toluidine Chloroferrite,*



$$\mathrm{FeCl_2.3C_6H_4}\!<\!\begin{array}{l}\mathrm{CH_3}\\ \mathrm{NH_3Cl.6H_2O}\end{array}$$

This salt was obtained only once when the analyses were reliable, though the analyses of another preparation pointed to the same salt with more water of crystallization. In all subsequent work the salt to be described later was obtained.

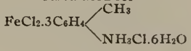
Three solutions were prepared. The first solution, in the ratio of 1 : 1, was composed of 10 cc. of a saturated solution of ferrous chloride, containing 4 grams of ferrous chloride, and a nearly saturated solution of 4.5 grams of *o*-toluidine hydrochloride. This solution, when heated and then allowed to cool, gave only *o*-toluidine hydrochloride.

The second solution, in the ratio of 2 : 1, was made by mixing 20 cc. of the saturated solution of ferrous chloride with a saturated solution of 4.5 grams of *o*-toluidine hydrochloride. From this ferrous chloride separated first; then a double salt. The double salt was dissolved by warming the solution and pouring off from the crystals of ferrous chloride.

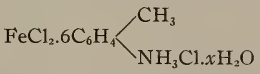
From the liquid a crop of yellow crystals separated in long, fine needles. The analyses of this sample did not give concordant results.

The third solution was composed of 12 grams of ferrous chloride in saturated solution and 4.5 grams of *o*-toluidine hydrochloride in saturated solution. This first gave ferrous chloride, then the mother liquor gave a mixture of the yellow needles, as obtained in the previous solution, with toluidine hydrochloride and crystals of a different yellow color.

Solution in the Ratio of 1 : 1.—As it was thought that these solutions did not contain enough acid, a second solution, in the ratio of 1 : 1, was prepared thus: Ten cc. of the saturated solution of ferrous chloride, containing 4 grams of ferrous chloride, was added to a solution of 4.5 grams of *o*-toluidine hydrochloride in 15 cc. of concentrated hydrochloric acid and 5 cc. of water. The solution was heated, and, when it was cooled, a crop of crystals formed which, when viewed on the ends, had a reddish yellow color, but, when viewed on the side, were of a light yellow color. Three grams of the dry salt were obtained. On analysis the salts gave the following results:

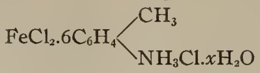
	Calculated for  $FeCl_2.3C_6H_4\Big\langle\begin{matrix}CH_3\\NH_3Cl.6H_2O\end{matrix}$	Found
Chlorine	26.62	26.36 26.68
Iron	8.42	8.00 8.37

Hexa-o-toluidine Chloroferrite,



$$FeCl_2.6C_6H_4\Big\langle\begin{matrix}CH_3\\NH_3Cl.xH_2O\end{matrix}$$

From solutions of ferrous chloride and *o*-toluidine hydrochloride in ratios varying from 2 : 1 to 1 : 4, ferrous chloride, toluidine hydrochloride and a double salt may separate, according to the condition of the experiment. In many cases a mixture of any two, or of all three of the substances, may be obtained. The analyses of the double salt—when the purity of the salt could be relied upon—in all cases, except the one already given, pointed to the compound of the formula



$$FeCl_2.6C_6H_4\begin{cases}CH_3\\NH_3Cl.xH_2O\end{cases}$$

In the first part of this work the solutions containing ferrous chloride and toluidine hydrochloride were boiled and cooled in beakers exposed to the air, so that, where there were second or third crops obtained from the mother liquors, these were found to be the *hexa-*o*-toluidine chloroferrate*, already described. Later the salt was made in an atmosphere of hydrogen.

Two solutions of ferrous chloride and *o*-toluidine hydrochloride were made up in the ratios of 2 : 1 and of 3 : 1. These solutions contained, respectively, 8 grams of ferrous chloride to 4.5 grams of *o*-toluidine hydrochloride, and 12 grams of ferrous chloride to 4.5 grams of *o*-toluidine hydrochloride; the volume was about 60 cc.

The 2 : 1 solution gave a crop of a double salt before the solution was quite cold. This was filtered off and prepared for analysis. Later a mixture of crystals of ferrous chloride and of a double salt was deposited.

The 3 : 1 solution gave a crop of the double salt that seemed to be free from impurities. It was analyzed.

A second solution in the ratio of 3 : 1 was made like that above; from this solution a salt was obtained. The analyses of these salts gave the following results:

		Found for salt from	
	Sol. 2 : 1	Sol. 3 : 1, No. I	Sol. 3 : 1, No. II
Chlorine	27.91	28.78	28.16
	27.92	28.77	28.14
		28.44	28.18
Iron	5.37	5.48	5.36
		5.42	5.39
Ratio of iron to chlorine	1 : 8.23	1 : 8.44	1 : 8.4

These salts gave ferrous hydroxide with potassium hydroxide.

Both of the mother liquors of the solutions in the ratio 3 : 1

gave crops of an orange salt, which, on analysis, proved to be hexa-*o*-toluidine chloroferrates.

In view of the results previously obtained in the investigation of double halides, this salt was entirely unexpected. Out of several hundred double halides that have been described this is the only one containing such a large proportion of the basic halide. Every effort was made to learn whether any deep-seated change takes place when ferrous chloride and *o*-toluidine are brought together, but the evidence all goes to show that the product is in fact a salt of the type $FeCl_2.6MCl$.[1]

REVIEWS

METHODS IN CHEMICAL ANALYSIS, Originated and Developed in the Kent Chemical Laboratory of Yale University. Compiled by FRANK AUSTIN GOOCH, Professor of Chemistry and Director of the Kent Chemical Laboratory in Yale University. New York: John Wiley & Sons; London: Chapman & Hall, Ltd. 1912. pp. xii + 536. Price, $4.00.

In the words of the author: "The object of this volume is to present concisely the principal results reached by workers in the Kent Chemical Laboratory of Yale University in the investigation and development of methods in chemical analysis. In the account of processes, modified or original, only proved procedure and immediately related experimental data are, as a rule, given."

No one can fail to be deeply impressed with this magnificent record of the achievements of the investigators in the Kent Chemical Laboratory in the field of analytical chemistry under the leadership of the compiler. Besides descriptions of many laboratory appliances and methods of general procedure, one or more methods for the estimation of no less than forty-seven elements are discussed. These include nearly all the common elements as well as some rare ones. The skill with which the gist of each investigation has been selected and the clearness with which it has been presented, together with the wide field covered, make the book invaluable to any one who is frequently confronted with new analytical problems.

One hesitates to criticize so admirable a production, but at any rate it is permissible to suggest that in the references the date of publication would sometimes be of assistance. While it is true that progress in analytical chemistry is made largely in the laboratory by process of trial, and while frequently the principle of a method turns out to be less simple than appearances at first indicate, so that theory must be adapted to fit the facts, yet on reading this book one cannot help regretting at times that the results are not discussed from the standpoint of the modern theory of solution. GREGORY P. BAXTER

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[1] Finding myself at present in a position to enable me to devote a large proportion of my time to chemical research, I am planning to review the whole subject of the double halides in the hope of getting further light upon the regularities in their composition, for, in spite of some irregularities, it is undoubtedly true that they show a strong tendency to conform to a few types as originally set forth by me in 1888 (THIS JOURNAL, 11, 291).—I. R.

A COLLEGE TEXT-BOOK OF QUANTITATIVE ANALYSIS. By HERBERT RAYMOND MOODY, S.B. (M.I.I.), A.M., PH.D. (COLUMBIA), Associate Professor of Analytical and Applied Chemistry, College of the City of New York. New York: The Macmillan Co. 1912. pp. vi + 165.

This book is intended for beginners and discusses a limited number of the more common quantitative methods. The chief emphasis is laid upon mechanical processes, with the idea of saving as much as possible of the instructor's energies by preventing mistakes on the student's part. The directions are therefore very complete. The author also lays stress on the intelligent employment of time in quantitative analysis.

Unfortunately, the scientific treatment of the subject is less satisfactory. As examples of the defects to which the book is subject, the following may be cited: The student is led to infer that weights may be determined with an accuracy of 0.1 milligram, yet no mention is made of the necessity of using calibrated weights; the student is told to wipe a weighing tube before weighing; handling a weighing tube with the fingers is directly implied. One cannot but question the advisability of giving, as the first quantitative experiment, the manipulation of so troublesome a substance as aluminium hydroxide. In the determination of silica, only one evaporation and filtration is prescribed. The solubility of precipitates is inadequately discussed, and the statement that nitric acid diminishes the solubility of silver chloride is obviously incorrect. The treatment of the subject of indicators leaves much to be desired. While the Gooch crucible is mentioned, no experiment is given which involves its use, and the Méker burner is nowhere described. Not only is the question of significant figures not discussed, but the use of figures is such as to lead to confusion in the mind of the student. For instance, 0.3795 gram of copper oxide is shown to yield 0.30322 gram of copper; 0.2500 gram of iron requires 31.18 cc. of permanganate solution, whence 1 cc. of permanganate is equivalent to 0.0080 gram iron; the following equation also occurs: $37.10 \times 0.0265 = 0.98315$. On page 138 the method of calculation is needlessly involved and necessitates multiplying and dividing by the molecular weight of hydrochloric acid. GREGORY P. BAXTER

THE VOLATILE OILS. By E. GILDEMEISTER and FR. HOFFMANN. Second Edition, by E. GILDEMEISTER. Written under the Auspices of the Firm of Schimmel & Co., Miltitz near Leipzig. Authorized translation by EDWARD KREMERS, Madison, Wis. First Volume. With Two Maps and Numerous Illustrations. New York: John Wiley & Sons, Inc. 1913. pp. xii + 677. Price, $5.00.

This book is divided into two distinct parts, historical and descriptive, the first of which remains substantially as written by Hoffmann for the first edition. This portion, occupying 241 pages, begins with a general history, from the earliest times, of the production, transportation and use of perfumes and aromatic substances. This is followed by a history of 87 of the best-known individual oils. This section concludes with a history of extraction and distillation processes from the crude apparatus and methods of antiquity to the giant stills of modern times. This is well illustrated with cuts of the older apparatus and full-page halftone pictures of some of the new.

Of the descriptive portion, 275 pages are devoted to an orderly enumeration and description of the chemical individuals that have been identified in volatile oils, together with a few compounds, such as ionone and the artificial musks, that may be classed with these. The treatment, particularly in the case of the more important substances, is very thorough, including the structural formula, occurrence, physical properties, chemical transformations, and means of identification. References to the literature are freely given. This is followed by a description of the methods of proximate analysis of volatile oils. Elaborate tables are given for the rapid calculation of analytical results. Some recent data have been inserted in the translation, which is well done.

The book is readable and interesting to the general reader in chemistry, while it serves as a convenient and comprehensive manual for the worker in the field. As might be expected in a book emanating from a commercial laboratory, great prominence is given to methods and products of that laboratory. The uninformed reader might even conclude that there is only one firm of importance in the large field. The firm and the authors deserve the thanks of the chemical public for a useful book.

E. EMMET REID

PRINCIPLES OF AGRICULTURAL CHEMISTRY. By G. S. FRAPS, PH.D., Associate Professor of Agricultural Chemistry, Agricultural and Mechanical College of Texas; Chemist, Texas Experiment Station; State Chemist. Easton, Pa.: The Chemical Publishing Co.; London: Williams & Norgate. 1913. pp. 493. Price, $4.00.

In this book the author has aimed to present the fundamental principles of agricultural chemistry from the point of view "of the chemist dealing with agricultural problems," also "to emphasize chemical methods of investigation, and to stimulate scientific habits of thought."

The matter which is presented is based upon a course of lectures given by the author for a series of years at the Agricultural and Mechanical College of the State of Texas. The book is divided into twenty-four chapters, two of which deal with the fundamental principles of plant nutrition and with the relation of the plant to the atmosphere. Ten chapters are devoted to the soil, embracing its origin, classification, water content, physical properties, chemical and physical composition, chemical changes, soluble constituents, active plant food, and its losses, gains and deficiencies. One chapter treats of farm manures, two of fertilizers, and two of the constituents and composition of plants. The closing chapters are given over to chemistry in its relation to animals, embracing one chapter each on digestion, and the calculation of feeding rations, and three chapters covering the fundamental chemical problems relating to animal nutrition.

The material in general is well arranged. The chapters on the origin, the physical character and the chemical constituents of soils will be found particularly valuable for students who have neither taken an extended course in the subject previously nor a course in elementary geology and mineralogy.

In the discussion of "soil deficiencies" the writer unfortunately cites certain experiments with ground limestone and burned lime, to show the superiority of the former, in which the burned lime was applied at the worst point in the rotation and in which lime was used in highly excessive amounts. He has thus created unintentionally an unwarranted prejudice against burned and slaked lime. The mass of material to be predigested by the author was obviously too great to permit him to make a careful individual analysis of all of the experiments cited.

In the chapter on the sources and composition of fertilizers the author has apparently neglected to mention, in making comparisons of prices of ready-mixed and home-mixed goods, the fact that the former are usually sold on long credit, often in less than ton lots, whereas the latter are often sold in carload lots for cash or on short credit, or if in small quantities essentially as bargain-counter transactions to insure the sale of other goods. Due attention should have been paid to the fact that under such conditions they do not bear their share of the "overhead" expenses. The chapter is replete, however, with most valuable suggestions concerning the precautions to be taken in the making of field experiments with fertilizers, and it contains much other most valuable matter.

The closing chapters give a very satisfactory review of the general subject of animal nutrition.

No attempt is made in this book to discuss exhaustively the various topics which are considered and this is left to special works on these subjects. It does nevertheless furnish to the student a splendid foundation for more extended study. The book meets this special need most admirably and it is also adapted to the large number of other readers who wish to secure a general survey of the field, without specializing particularly in any one direction. For the purposes which have been mentioned this book appears to be better adapted to American needs than any heretofore published in this country or in England. The author is to be congratulated on his timely and meritorious production, and the book will be cordially welcomed by all who are interested in agricultural progress in the United States.

H. J. WHEELER

CYANAMID, Manufacture, Chemistry and Uses. By EDWARD J. PRANKE, B.Sc. Easton, Pa.: The Chemical Publishing Co. 1913. pp. vi + 112. Price, $1.25.

This book deals with the discovery, manufacture, preparation, properties and storage of cyanamide, its decomposition in the soil, use as a fertilizer and in mixed fertilizers, and with other topics relating to the subject. The book contains a number of references, and some original work of the author. The subject is fully treated. The book can be recommended to those who desire to become familiar with the subject.

G. S. F.

A FOUNDATION COURSE IN CHEMISTRY FOR STUDENTS OF AGRICULTURE AND TECHNOLOGY. By J. W. DODGSON, B.Sc. (LOND.), Lecturer in Chemistry at University College, Reading, and J. ALLAN MURRAY, B.Sc. (EDIN.), Lecturer in Agricultural Chemistry at University College, Reading. With Diagrams. London, New York, Bombay and Calcutta: Longmans, Green & Co. 1913. pp. x + 243. Price, $1.10.

This book is intended for students attending short courses in agriculture, for those taking education courses in hygiene and domestic economy, and in fact for all who take up the study of chemistry as a preliminary to some technical or commercial pursuit. The book devotes space both to inorganic and organic chemistry. It has chapters headed air, water, limestone, ashes, sand, clay, etc., organic matter, paraffins and their derivatives, coal tar, some common metals. The author states that the book is based upon courses of lectures given during a number of years. It contains a large number of chemical reactions, and many structural formulas, including one for silicic acid. G. S. F.

THE POLYTECHNIC ENGINEER. Published annually by the STUDENTS OF THE POLYTECHNIC INSTITUTE OF BROOKLYN. Vol. XIII. 1913. pp. 138.

The students of the Brooklyn Polytechnic Institute have good reason to be proud of their Annual. The typography, illustrations and binding are all that could be desired. The present volume is dedicated to Professor Samuel Sheldon, of the Physics and Electrical Engineering Department. Of interest to chemists may be mentioned the articles on the Thickness of Films of Silver upon Glass, by Irving W. Fay and Arthur C. Rauchfuss; The Industries of Detroit, by John C. Olsen; Blue and Iridescent Gelatine-Copper, by Frederick W. Moe, Jr.; Chinese Wood Oil, by Everitt J. Cole; and Résumé of the Lectures delivered by Sir William Ramsay at the Institute on Oct. 22, 29, and Nov. 5, 1912. C. A. R.

LOGARITHMIC REDUCTION TABLES for Students of Analytical Chemistry. By CHARLES J. MOORE, PH.D. (VIRGINIA), Austin Teaching Fellow in Advanced Analytical Chemistry in Harvard University. Boston, New York, Chicago, London: Ginn & Company. pp. viii + 78. Price, $1.00.

This useful little book contains 28 tables of the numerical constants and factors most frequently made use of in analytical chemistry, together with the corresponding logarithms. A six-place table of logarithms is also given, followed by brief explanatory directions for the use of the various tables. The type is exceptionally clear and this little book should prove very useful. C. A. R.

SPECIAL ANNOUNCEMENT

By an agreement with the Directors of the American Chemical Society, THIS JOURNAL will be discontinued as a separate publication on the completion of the 50th volume and, beginning January, 1914, will be incorporated with the Journal of the Society. A fuller statement in regard to the consolidation will appear in the December number.

VOL. L DECEMBER, 1913 No. 6

AMERICAN

CHEMICAL JOURNAL

[Contributions from the Chemical Laboratory of Harvard College]

THE ACTION OF SODIC HYDROXIDE ON TETRABROMORTHOBENZOQUINONE[1]

BY C. LORING JACKSON AND A. H. FISKE

In his wonderfully comprehensive paper[2] on tetrabromorthoquinone, Zincke states that a solution of sodic hydroxide converts it into an unstable green solid, which afterwards dissolves, forming the sodium salts of tetrabrompyrocatechin and what is probably a cyclopentenecarboxylic acid. A more detailed study of these reactions has shown the accuracy of his observations, although the action is not quite so simple as he thought.

The green solid formed at first decomposes spontaneously on standing with the alkali, or, if filtered out, as soon as it dries; and this instability, with its marked color, suggests that it may be closely related to the green or blue compounds[3] which have been frequently observed when alkaline substances act on quinones. Torrey and Hunter have given reasons for supposing that some, at least, of these products are salts of quinhydrones, and the properties of our green solid were not at variance with this hypothesis. For instance, it yielded on acidification a mass easily soluble in alcohol, like the mixture of tetrabrompyrocatechin and tetrabromorthoquinone which would be formed from a quinhydrone; and the brown product formed by its spontaneous decomposition, although it resembled in appearance the ether $C_6Br_4O_2C_6Br_2(OH)_2$, was also too soluble in alcohol to be this compound. It was probably the expected mixture of tetrabrompyrocatechin and tetrabromorthoquinone, since the ether $C_6Br_4O_2C_6Br_2O_2$ was formed when it was treated with glacial acetic acid. According to the views developed later, if the green substance is the salt of the octobromorthoquinhydrone, its formation is due to a secondary reaction, and it is of no use in tracing the decomposition of tetrabromorthoquinone by sodic hydroxide and this is also true if we adopt the theory of Astre or of Richter.

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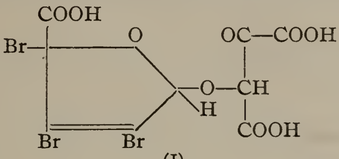
[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the Degree of Doctor of Philosophy by Augustus Henry Fiske.

[2] Ber. d. chem. Ges., **20**, 1776 (1887).

[3] Barth, Schreder: Monats. Chem., **4**, 176 (1883). Hantzsch, Herman: Ber. d. chem. Ges., **21**, 1754 (1888). Sworer: Chem. News, **60**, 1887 (1889). Nietzki, Schmidt: Ber. d. chem. Ges., **22**, 1653 (1889). Mazzara: *Ibid.*, **23**, 1390 (1890). Kehrmann: J. prakt. Chem., [2] **43**, 260 (1891). Jackson, Grindley: THIS JOURNAL, **17**, 655 (1895). Astre: Compt. rend., **121**, 326, 530 (1895). Jackson, Torrey: THIS JOURNAL, **20**, 426 (1898). Imbert: Compt. rend., **126**, 529 (1898). Fischer, Wellmann: Ber. d. chem. Ges., **37**, 2384 (1904). Torrey, Hunter: J. Am. Chem. Soc., **34**, 705 (1912). Richter: Ber. d. chem. Ges., **43**, 3599 (1910).

To detect the real products of the action of sodic hydroxide on tetrabromorthoquinone we took up the study of the yellowish solution obtained by the further action of the alkali upon the green solid, which was the first product. This yielded on acidification a precipitate of tetrabrompyrocatechin, as already found by Zincke, and after this had been filtered off, extraction with ether gave an acid which differed according to the strength of the solution of sodic hydroxide used. A normal solution produced an acid melting at 217°, to which we assign provisionally the formula $C_{10}H_6Br_4O_9$. With a solution containing 60 grams to the liter two acids were obtained, one, $C_{10}H_5Br_3O_9$, melting at 207°, and one at 121°, of which we have as yet only bromine determinations, so that we give the formula $C_{10}H_5Br_5O_7$ with all possible reserve. Finally, with a solution containing 200 grams of sodic hydroxide in the liter the acid melted at 174°, and had the formula $C_{11}H_6Br_2O_9$. Of these acids only that melting at 207° has been studied with any approach to thoroughness, so we begin our discussion of their structural relations with this compound.

Our attempts to make out the constitution of the acid $C_{10}H_5Br_3O_9$ melting at 207° have led to four structural formulas in harmony with the observed facts. Of these, Formula I explains the observations most simply, and we have therefore adopted it as the best expression of our present knowledge of this compound, but much more experimental work will be necessary before its structure is finally established.



(I)

The other formulas, which require more strained hypotheses to bring them into harmony with the facts, will be discussed after we have given our reasons for preferring Formula I. According to this view of its structure the acid is the tribromcarboxylketocyclopentene ether of oxalhydroxyacetic acid.

One of the strongest arguments for Formula I is that such a compound would be produced by the action of sodic hydroxide on tetrabromorthoquinone by a series of reactions, each of which is the one to be expected under such conditions; we shall therefore give these reactions in detail. In forming an acid with 10 atoms of carbon from tetrabromorthoquinone, $C_6Br_4O_2$, two molecules of this substance must be united in some way, and the most probable attachment is one by the oxygen forming in the first place the ether $C_6Br_4O_2C_6Br_2O_2$, which is easily produced by the action of tetrabrompyrocatechin on tetrabromorthoquinone. We are here met with the difficulty of forming the small amount of tetrabrompyrocatechin necessary to start Reaction I. After the reactions have begun, more than enough of this body will be formed to continue the action to an end; in fact, as already stated, a considerable excess of it is left after the reactions are finished. We have tried to meet this difficulty by supposing a reaction similar to that of sodic hydroxide on benzaldehyde, giving the tetrabrompyrocatechin needed and some acid, but, as this first action will be superseded at once by Reactions I–IX, this suppositious acid will be formed in such small quantity that it would naturally be overlooked among the secondary products, unless, indeed, it was decomposed by further action of the sodic hydroxide. The tetrabrompyrocatechin for starting Reaction I once obtained, the acid with Formula I is produced as follows:

I. $C_6Br_4(OH)_2 + C_6Br_4O_2 + 2NaOH = C_6Br_4O_2C_6Br_2O_2 + 2NaBr + 2H_2O$

II. $C_6Br_4O_2C_6Br_2O_2 + 4NaOH + C_6Br_4O_2 = C_6Br_4O_2C_2(CBrCOONa)_2 + C_6Br_4(ONa)_2 + 2H_2O$

III. $C_6Br_4O_2C_2(CBrCOONa)_2 + 2NaOH = C_6Br_4O_2C_2[C(OH)COONa]_2 + 2NaBr = C_6Br_4O_2C_2H_2(COCOONa)_2 + 2NaBr$

IV. $C_6Br_4O_2C_2H_2(COCOONa)_2 + 2NaOH = C_6Br_4O_2C_2H_2(CHO)_2 + 2Na_2CO_3$

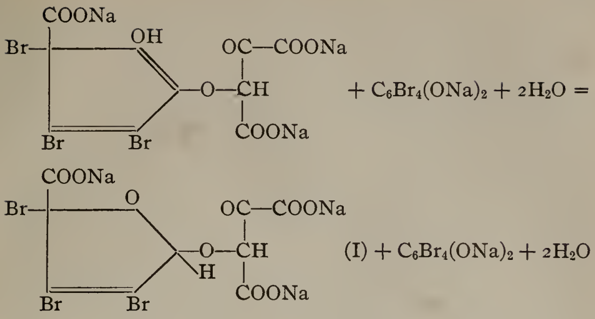
V. $C_6Br_4O_2C_2H_2(CHO)_2 + 6NaOH + 2C_6Br_4O_2 = C_6Br_4O_2C_2H_2(COONa)_2 + 2C_6Br_4(ONa)_2 + 4H_2O$

VI. $C_6Br_4O_2C_2H_2(COONa)_2 + NaOH = (C_6Br_4OH)OCH(COONa)CH(ONa)COONa$

VII. $(C_6Br_4OH)OCH(COONa)CH(ONa)COONa + NaOH + C_6Br_4O_2 = (C_6Br_4OH)OCH(COONa)COCOONa + C_6Br_4(ONa)_2 + H_2O$

VIII. $(C_6Br_4OH)OCH(COONa)COCOONa + NaOH = (C_6Br_3O_2H_2)OCH(COONa)COCOONa + NaBr$

IX. $(C_6Br_3O_2H_2)OCH(COONa)COCOONa + 3NaOH + C_6Br_4O_2 = NaOCOCBrHCBr{:}CBr.C({:}COH)OCH(COONa)COCOONa + C_6Br_4(ONa)_2 + 2H_2O =$



Some quantitative experiments which give a certain amount of support to these reactions, and a possible objection to Reaction II, will be discussed near the end of this introduction.

The second argument in favor of Formula I is based on the most striking reaction of our acid, that of bromine on a strong aqueous solution of it, which yielded 3 molecules of carbonic dioxide for each molecule of the acid, a little oxalic acid, and a substance melting at 97°–98°. The 3 molecules of carbonic dioxide would be expected from the decomposition of the 3 carboxyl groups in Formula I, and the oxalic acid would be the natural product from the two atoms of carbon remaining in the oxalhydroxyacetic side chain, after it had lost its two carboxyls. The amount of oxalic acid obtained was smaller than would be expected on this theory, but this is accounted for by its decomposition during the evaporation of the solution containing an excess of bromine.[1] The substance melting at 97°–98° was proved to be the heptabrommethyldiacetyl, $CBr_3CHBrCOCOCBr_3$, which would be formed from an acid with Formula I by the introduction of 4 atoms of bromine between the two atoms of carbon now carrying bromine alone, the loss of carbonic dioxide by the carboxyl groups and the removal by oxidation of the residue left after the destruction of the side chain.

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[1] No attempt was made to collect any carbonic dioxide formed during this evaporation, the 3 molecules of carbonic dioxide mentioned above being given off during the reaction in the cold.

The proof that the substance melting at 97°–98° had the formula $CBr_3CHBrCOCOCBr_3$ was given by the action of sodic carbonate in aqueous solution upon it, which yielded 2 molecules of bromoform, one of sodic oxalate, and one of sodic bromide for each molecule of the substance. We also expected formaldehyde or formic acid from the —CHBr— group, but were unable to find it in spite of many attempts. When the substance was heated to 100° in a sealed tube with water, an organic compound described later was the principal product, and small amounts of bromoform, hydrobromic acid, and oxalic acid were formed, showing a decomposition similar to that with sodic carbonate, but it was of especial interest that in this case they were accompanied by carbonic dioxide, probably resulting from the —CHBr— group, whose decomposition product had escaped us in the experiments with sodic carbonate, as must have been the case if it consisted of carbonic dioxide.

When trying to identify the bromoform obtained in this reaction we were confronted with one of those cases not uncommon in organic research, where it is necessary to study a liquid that can be prepared in quantity sufficient for the ordinary methods of manipulation only with a great expenditure of time and labor. For instance, if we dried our specimen (obtained from several experiments) with a dehydrating agent, the loss would reduce it below the amount necessary for analysis, and drying *in vacuo* was impossible because of its volatility. Accordingly, we used successfully the method of drying by wiping with moist filter paper devised by us[1] for such cases. Again, it was impossible with so little substance to obtain a boiling point accurate enough to characterize it, and to meet this difficulty a method of identification was contrived by one of us (Fiske), which gave an excellent result even with this small quantity, and so far as we can find is new. It seems to us a valuable addition to the resources of the organic chemist in cases of this sort. The process consists in determining the vapor pressure of the oily liquid by distilling it with a few drops of water, and observing the boiling point, which can be determined with sufficient accuracy with this larger amount of liquid. The vapor pressure of water at this temperature was then subtracted from the barometric pressure, leaving the vapor pressure of the other liquid, which was compared with that calculated for the supposed compound. In our experiment the boiling point was found to be 93°–94°, which gave as the vapor pressure of the oil 163 mm., while the vapor pressure of bromoform at 93°–94° was determined from the observations of Kahlbaum and Thorpe to be between 162 and 164 mm.

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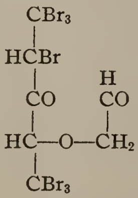
[1] This Journal, **44**, 439 (1910).

Our inference that the substance melting at 97°–98° is the heptabrommethyldiacetyl was confirmed by its showing the yellow color characteristic of 1,2-diketones, which disappeared when a derivative was formed affecting the keto groups, such as, for instance, the hemiacetals with alcohols. Other confirmatory observations were the formation of oxamide when the body was treated with ammonia, of oxanilide with aniline, and of ethyl oxalate, probably the mono ester, when the ethyl hemiacetal was decomposed by water at 100°. On the other hand we could obtain neither an oxime nor a hydrazone from this diketone, but that is not strange, as these reactions generally fail with ketones loaded with negative radicals.

In addition to the two principal arguments for assigning Formula I to the acid melting at 207° the following observations tell in favor of this formula. By the less energetic action of bromine and water on the acid a product melting at 96°–97° is obtained, which upon analysis gave results corresponding to the formula

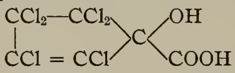


$$\begin{array}{ccc} \mathrm{CBr_3} & & \\ | & & \\ \mathrm{HCBr} & & \\ | & & \mathrm{H} \\ \mathrm{CO} & & \mathrm{CO} \\ | & & | \\ \mathrm{HC} & \text{—O—} & \mathrm{CH_2} \\ | & & \\ \mathrm{CBr_3} & & \end{array}$$

(II)

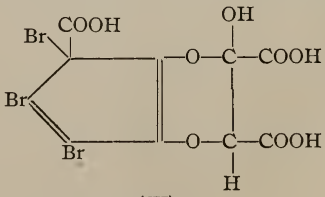
Unfortunately we have not had time to test this structure by further experiments, but two observations give it a certain confirmation. The substance is white instead of being yellow like the heptabrommethyldiacetyl, and on exposure to the air it turns brown, which may be due to an oxidation of the aldehyde group. Sodic carbonate in aqueous solution causes the replacement of one of the atoms of bromine by a hydroxyl group, giving a compound, $C_7H_6Br_6O_4$, melting at 71°–72°, instead of decomposing it completely, as it does the substituted diacetyl.

The acid melting at 207° is tribasic as required by Formula I, and its salts are so unstable that they are decomposed even by the spontaneous evaporation of their aqueous solutions, as would be expected from a derivative of the yet unprepared oxalhydroxyacetic acid. Also the difficulty in isolating these salts recalls the experience of Zincke and Kuster[1] with the acid



which in some respects is like the cyclopentene ring of Formula I. We succeeded in preparing in a pure state only the monopyridine salt made without the use of water, and it is worth noting that our formula shows a difference between one of the carboxyls and the other two, which might well lead to a mono salt. In fact, our observations agree with Formula I with the single exception that boiling the acid with strong hydrobromic acid for 8 hours leaves it unaltered.

In addition to Formula I we have worked out three others, which explain the reactions of our acid melting at 207°, but



(III)

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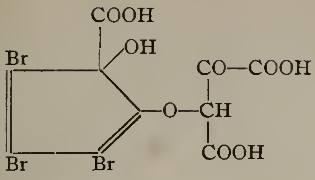
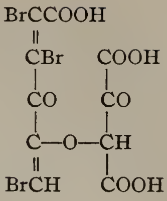
[1] Ber. d. chem. Ges., **21**, 2719; **23**, 812.



(IV)



(V)

we prefer (I) for the following reasons: It seems to us that the hydroxyl group in (III) could be formed only by a much less probable reaction then any of those given in Reactions I–IX, and, further, such a compound should give an acet derivative with acetyl chloride, whereas our acid is not affected by this reagent. (IV) is attractive from its analogy to the cyclopentenehydroxy acids usually formed by the breaking down of a six-carbon ring,[1] but it shares with (III) the objection that it should form an acet compound, and also it is probable that with bromine and water it would give $CBr_3CBr_2COCOCBr_3$ rather than the actual product $CBr_3CHBrCOCOCBr_3$. To be sure, this compound could be formed, if hydrobromic acid were added as well as bromine, but this seems to us improbable when bromine, as here, is in great excess. This last objection also applies to (V) and the conversion of the $CHBr_2$ groups into CBr_3 makes the decomposition of such a body with bromine and water less simple than that of one constituted as in Formula I. It will be observed that none of these objections are strong enough to lead to the rejection of these formulas, but they seem to us to leave (I) as the simplest explanation of the observed facts, which is all we claim for it.

The heptabrommethyldiacetyl, $CBr_3CHBrCOCOCBr_3$, combines with methyl alcohol in the cold to form the monomethyl hemiacetal, $CBr_3CHBrC(OH)(OCH_3)COCBr_3$, melting at 100°–101°; and with ethyl alcohol the corresponding compound, $CBr_3CHBrC(OH)(OC_2H_5)COCBr_3$, melting at 93°–94°. The position of the hemiacetal group has not been determined. The ethyl compound, when heated with water to 100° in a sealed tube, yielded an oil, which, after it had been freed from bromoform, distilled at about the boiling point of diethyloxalic ester, and therefore was probably the expected monoethyl ester, which is converted into the diethyl compound by distillation.

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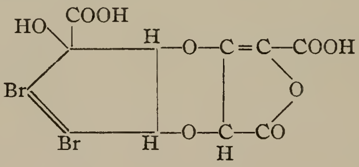
[1] For instance, Zincke: Ber. d. chem. Ges., **19**, 2509 (1886). Zincke, Kuster: *Ibid.*, **26**, 2104 (1893).

Of the three other acids, that melting at 174° has been the most thoroughly studied, and, although the work has not gone far, we have discovered a formula for it which accounts for the known facts and agrees so well with that proposed for the acid melting at 207° that we feel justified in adopting it provisionally, although we can bring no proof of its correctness. This acid melting at 174° has the formula $C_{11}H_6Br_2O_9$, and when treated with bromine and water gives the heptabrommethyldiacetyl obtained from the acid melting at 207°; it is fair to assume, therefore, that both contain a similar group, the five-carbon ring of Formula I. From this assumption the structure (VI) is easily developed, in which the side chain consists of a carboxyllactone, and the substance is the dibromhydroxycarboxylcyclopentene orthodiether of carboxyldihydroxyisocrotonlactone. It was proved to be tribasic by titration with sodic hydroxide, which might well saponify such a lactone, whereas with baric carbonate the salt of a dibasic acid was obtained, in harmony with Formula VI. The salts of this acid were unstable like those of the acid melting at 207° and this would be expected of (VI), on the one hand in view of the work of Zincke and Kuster cited above, and on the



(VI)

other since the lactone on saponification would give an unsaturated hydroxyl acid dropping at once into a comparatively unstable α-keto acid. In forming the heptabrommethyldiacetyl from it by the action of bromine and water the action would be similar to that already given under the acid melting at 207°, with the addition of the conversion of the hydroxyl into bromine by the hydrobromic acid formed in the previous reactions. The lactone might well resist the milder action of bromine, and therefore not give the white compound $CBr_3CHBrCOCH(OC_2H_3O)CBr_3$, melting at 96°–97°, obtained in this way from the 207° acid.

The formation of an acid of Formula VI from tetrabromorthoquinone may be explained by reactions similar to I–IX, on the supposition that the more reactive stronger alkali carries the action on one branch of the side chain (Reactions III, IV, V) to the formation of the final carboxyl group, before the second branch has had time to be attacked, giving the compound $C_6Br_4O_2C_2H(:CBrCOONa)(COONa)$, when the lactone would be formed by the reaction of the sodium in the COONa group with the bromine in the γ position.

We can say little about the constitution of the two remaining acids. Even the empirical formula of that melting at 121° is still doubtful, as the mother liquors, in which it was found occasionally, yielded enough of it only for some determinations of bromine. The formula of the acid melting at 217° rests on a safer basis, as the bromine determinations were confirmed by a determination of calcium in the calcium salt, which also showed the acid to be dibasic. While more analytical work is necessary before the formula $C_{10}H_6Br_4O_9$ can be finally accepted, we have observed a few facts which throw some light on its constitution. It is distinctly whiter than the two acids melting at 207° and 174°, and, when treated with bromine and water, it gave a white substance melting at 156° instead of the yellow heptabrommethyldiacetyl melting at 97°–98°; we therefore think it probable that it does not contain the cyclopentene group of Formulas I and VI, but that in it the benzene ring may exist unaltered, and this view is supported by the large amount of bromine (4 atoms) which it contains, and the fact that it is formed when weak solutions of the alkali are used.

Whenever the decomposition of the tetrabromorthoquinone was carried on with a weak solution of sodic hydroxide, an oil appeared in addition to the solid acids. We did not have time to attempt the identification of this oil—at best a very difficult task—but a series of quantitative experiments with a fifth-normal solution of potassic hydroxide may throw some light on its relationships. In the following table the experimental results ("Found") are compared with the amounts of potassic hydroxide, carbonic dioxide and potassic bromide required by Reactions I–IX ("Calculated"). The quantities are given in numbers of molecules.

	Calculated		Found	
$C_6Br_4O_2$	7			
KOH	22	24.0	22.92	23.18
CO_2	2	2.62	1.84	1.85
KBr	5		14.3	14.3

The agreement between these experimental results is much closer than we expected, considering possible secondary reactions, and, if it is not due to accidental coincidences, seems to us to justify the conclusion that the two products (the acid melting at 217° and the oil) are formed principally by the same series of reactions, for, if there were two parallel series, it is hardly possible that such close agreements would be obtained in three series of experiments, in which no special care was taken to secure the same conditions. The agreement of the observed amounts of potassic hydroxide and carbonic dioxide with those required by Reactions I–IX for making the acid melting at 207° would indicate that the series of reactions mentioned above is identical with these so far as the use of potassic hydroxide and the formation of carbonic dioxide are concerned, the acid melting at 217° proceeding from only part of them, and the oils probably being formed from the two solid acids by the replacement of bromine, owing to the action of the potassic tetrabrompyrocatechin present in large quantity in the solution, thus forming the excess of potassic bromide, which amounts to nearly 3 times that given by the formation of the acid melting at 207°. The agreement between the observed quantities and those required for Reactions I–IX except in the case of the potassic bromide furnishes a welcome confirmation of these reactions.

Some experiments with tetrabromorthoquinone and reagents other than sodic hydroxide showed that potassic or ammonic hydroxide acted in essentially the same way as sodic hydroxide; baric hydroxide seemed to give only the differences to be expected from the insolubility of the barium salt of tetrabrompyrocatechin, but plumbic hydroxide had no action. Sodic or acid sodic carbonate also seemed to behave like sodic hydroxide, giving the unstable green product, some of the acids described above, and in addition bromanilic acid. At first we supposed this new product to be formed from the tetrabrompyrocatechin, but this could not be the case, as special experiments showed that this compound is not decomposed under any conditions by solutions even of sodic hydroxide weaker than twice normal, and this twice normal solution forms bromanilic acid with it only when boiling. On the other hand the red ether $C_6Br_4O_2C_6Br_2O_2$ yields bromanilic acid with a twice normal solution of sodic hydroxide after standing for two days in the cold, so that here is the probable source of this product in the experiments mentioned above. This action, however, is a slow one, as even after heating tetrabromorthoquinone with a solution of sodic hydroxide for an hour there was left 1 gram of the ether $C_6Br_4O_2C_6Br_2O_2$ from 5 grams of the orthoquinone.

In Reaction II we represent the red ether as decomposed by sodic hydroxide in a different way from the saponification mentioned above, but we think this difference is sufficiently explained by the presence of the oxidizing agent (tetrabromorthoquinone). Under these circumstances Reaction II might take place so much more rapidly than the rather sluggish saponification of the ether that no bromanilic acid would be formed. This hypothesis is supported by the fact that the bromanilic acid appears as a secondary product only, when the reactions are carried on with milder alkaline reagents, such as baric hydroxide, sodic carbonate, or acid sodic carbonate, which need to stand for some time with the tetrabromorthoquinone to form our acids.

EXPERIMENTAL

ACTION OF ALKALINE SOLUTIONS ON TETRABROMORTHOBENZOQUINONE

The Green Preliminary Product

The first visible effect of an alkaline solution on tetrabromorthoquinone was the formation of a green solid, which, however, was very unstable, as, if sodic hydroxide was used, it disappeared often in as short a time as 10 minutes, forming a yellowish liquid. With a solution of sodic carbonate the green product acted less quickly, some specimens retaining their color for as much as two days, but finally, in this case, also, it decomposed partly into the yellowish solution, partly into a brown solid. In trying to prepare the green substance we used, therefore, a half normal solution of sodic carbonate with the tetrabromorthoquinone dissolved in benzene and poured upon the alkaline liquid. A green line soon appeared at the junction of the two liquids, and the precipitate, as it formed, fell through the aqueous liquid, and collected on the bottom of the vessel. The product obtained in this way was free from imprisoned tetrabromorthoquinone, which was always present, when, as in most of our experiments, the alkaline liquid acted on the solid quinone. A green specimen (containing imprisoned orthoquinone) was filtered out, washed with a little water, which removed bromanilic acid, and allowed to dry on a porous plate. As soon as it became fairly dry, brown spots appeared, which gradually spread throughout the entire mass. This behavior recalls the sodium salt of tribromresorcin,[1] which decomposed spontaneously in a similar way. A portion, which had not lost its green color, was acidified with hydrochloric acid, when it was converted into a reddish brown solid easily soluble in alcohol. Of the products which would be expected from this reaction, this solubility is in harmony with tetrabromorthoquinone and tetrabrompyrocatechin, whereas the ethers $C_6Br_4O_2C_6Br_2O_2$

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[1] This Journal, **18**, 117 (1896).

and $C_6Br_4O_2C_6Br_2(OH)_2$ could hardly be present, as they are only slightly soluble in alcohol.

We also tried the following experiments on the brown solid formed by the spontaneous decomposition of the green product. A specimen of it dissolved freely in alcohol, and water threw down from the solution a dull reddish brown precipitate. Another specimen, prepared by the benzene method, and therefore free from imprisoned orthoquinone, was washed with water, to which it gave up a quantity of sodic bromanilate, and then treated with hot glacial acetic acid, which dissolved most of it, but left a residue, evidently the ether $C_6Br_4O_2C_6Br_2O_2$ from its brilliant red color and essential insolubility in common solvents. The acetic acid solution contained much tetrabrompyrocatechin. These observations indicate that the brown product is principally tetrabrompyrocatechin with some tetrabromorthoquinone, and this view is supported by the observation that much of the ether $C_6Br_4O_2C_6Br_2O_2$ was formed by the action of nitric acid on the brown product. Neither the red ether $C_6Br_4O_2C_6Br_2O_2$ nor the brown one $C_6Br_4O_2C_6Br_2(OH)_2$ can exist in any quantity already formed in this brown substance, because, as stated earlier, it is easily soluble in alcohol.

Final Products of the Action of Sodic Hydroxide

After the green solid formed at first had disappeared, the product of the action of sodic hydroxide on tetrabromorthoquinone was a slightly yellow solution, and this on acidification with hydrochloric acid deposited a precipitate, which, as Zincke[1] states, is tetrabrompyrocatechin, since on recrystallization from hot glacial acetic acid it showed the constant melting point 190°–191° instead of 191°–192° and an analysis gave 75.39 per cent. of bromine, whereas $C_6Br_4(OH)_2$ contains 75.11 per cent. Further, when treated in alcoholic solution with fuming nitric acid and glacial acetic acid, it gave a red crystalline product melting at 146°–147°, the melting point of the crude tetrabromorthoquinone prepared in this way, and sodic hydroxide gave with this the characteristic green color.

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[1] Ber. d. chem. Ges., **20**, 1776 (1887).

The filtrate from the tetrabrompyrocatechin gave on extraction with ether one or more acids, the product differing according to the conditions under which it was formed; thus, a normal solution yielded an acid melting at 217°; from one containing 60 grams of sodic hydroxide in the liter two acids were obtained, one melting at 207°, the other at 121°; while, if the solution contained 200 grams of sodic hydroxide in the liter, the resultant acid melted at 174°. These were the usual products when solutions of the strength given were used, but on 3 occasions exceptional results were obtained; thus, once a solution containing 200 grams of sodic hydroxide to the liter gave almost entirely the acid melting at 207° instead of that melting at 174° (we cannot explain this, unless it were due to the difference in temperature between winter and spring); and on two occasions the acid melting at 174° was obtained with the weaker solutions, which usually gave the other acids; of these one was with a half normal solution cooled to 4°; the other was when a half normal solution was used with a benzene solution of tetrabromorthoquinone instead of with the dry powder.

An account of our study of the effects of other conditions and reagents on the product will be found after the descriptions of the four acids, which we begin with that melting at 207°, as this is the only one which we have been able to study at length in the time at our disposal.

Acid Melting at 207°. Tribromcarboxylketocyclopentene Ether of Oxalhydroxyacetic Acid

Twenty grams of tetrabromorthoquinone were mixed with one liter of a solution containing 60 grams of sodic hydroxide, and the mixture allowed to stand at the temperature of the room with occasional shaking, till all of the green precipitate formed at first had dissolved. The solution was then poured into a beaker containing a little more than the amount of strong hydrochloric acid required for the neutralization of the alkali, and the precipitate allowed to settle overnight, as this facilitated the filtration. After this tetrabrompyrocatechin had been removed, the filtate was extracted with ether most conveniently in the apparatus invented by one of us.[1] The ether extract on spontaneous evaporation left a yellow crystalline residue mixed with an oil (discussed later in this paper), and this, after standing on a porous plate, was boiled repeatedly with successive portions of benzene, from which on cooling the acid separated as a yellow flocculent precipitate. It was washed with cold benzene, and then purified by recrystallization from hot benzene, until it showed the constant melting point 207°, when it was dried *in vacuo* for analysis.

I. 0.3383 gram substance gave 0.2930 gram CO_2, 0.0343 gram H_2O.

II. 0.2258 gram substance gave 0.1961 gram CO_2, 0.0237 gram H_2O.

III. 0.1330 gram substance gave 0.1477 gram AgBr.

IV. 0.2224 gram substance gave 0.2460 gram AgBr.

	Calculated for $C_{10}H_5Br_3O_9$	Found			
		I	II	III	IV
C	23.58	23.62	23.69		
H	0.98	1.13	1.17		
Br	47.16			47.25	47.06

Properties of Tribromcarboxylketocyclopentene Ether of Oxalhydroxyacetic Acid.—It crystallizes from benzene in flocculent masses of pale yellow needles, which melt with decomposition at 207°. It is easily soluble in water, alcohol, methyl alcohol, ether, chloroform, ethyl acetate or glacial acetic acid, slightly soluble in cold benzene, more freely in hot, almost insoluble in ligroin. Benzene is the best solvent for it. The aqueous solution decomposes carbonates with effervescence. The basicity of the acid was determined by titration with fifth-normal potassic hydroxide solution, phenolphthalein being used as the indicator.

I. 0.3258 gram substance required 10.24 cc. of the solution containing 0.0800 gram K.

II. 0.6687 gram substance required 20.88 cc. containing 0.1633 gram K.

	Calculated for $C_{10}H_2Br_3K_3O_9$	Found	
		I	II
K	19.11	19.70	19.63

The acid is therefore tribasic.

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[1] Fiske: This Journal, **41**, 510 (1909).

Many attempts were made to prepare salts of the acid, but none were obtained in a pure state except a monopyridine salt described later. The solutions prepared by the action of the acid on a hydroxide or carbonate decomposed on evaporation, as shown by the appearance of a brown color, even when the evaporation was carried on at ordinary temperatures. The sodium salt and the calcium salt prepared from the carbonates gave no products worth analysis. The barium salt was prepared from the hydroxide and acid in aqueous solution, removing the excess of baric hydroxide with carbonic dioxide, and heating to drive off the excess of carbonic dioxide. The filtrate was then allowed to evaporate spontaneously, and the salt analyzed.

0.0910 gram of salt gave 0.0468 gram $BaSO_4$.

	Calculated for $Ba_3(C_{10}H_2Br_3O_9)_2$	Found
Ba	28.97	30.24

This, so far as it goes, confirms the results from the titrations.

An attempt to prepare an ammonium salt with aqueous ammonic hydroxide gave what seemed to be a compound $C_{10}H_2(NH_4)_3Br_2NH_2O_9$, the bromine found differing from the theoretical by about 2 per cent.

We next tried to prepare salts without the use of water. On dissolving the acid in an excess of pyridine, and diluting with ether, yellow, feathery flakes were precipitated, which, after thorough washing with ether, melted at 122°–123°, and were dried *in vacuo* for analysis.

I. 0.1168 gram substance gave 0.1113 gram AgBr.

II. 0.1005 gram substance gave 0.0943 gram AgBr.

	Calculated for $C_{10}H_5(C_5H_5N)Br_3O_9$	Found	
		I	II
Br	40.82	40.54	39.94

The substance is therefore the monopyridine salt. It forms yellow, feathery flakes which melt at 122°–123°, and are insoluble in ether or benzene.

A phenylhydrazine salt made by mixing benzene solutions of the acid and phenylhydrazine came down as a pale yellow precipitate, but gave results on analysis between those for a mono and a di salt.

Aniline had no apparent action on a benzene solution of the acid. Sodic methylate seemed to have no action in the cold, as no sodic bromide was formed, but if heated with the acid, a test for bromide was obtained. When the acid was boiled with a twice normal solution of sodic hydroxide, a dark reddish solution was obtained, which gave a test for sodic bromide. In the time we could give to this work we did not succeed in isolating the organic product, but on treating the solution with bromine and water a yellow precipitate was formed, which after purification melted at 97°, and was therefore undoubtedly the heptabrommethyldiacetyl, formed by the action of bromine and water on the original acid melting at 207° as described later. The sodic hydroxide therefore seems not to have effected a far-reaching decomposition, but to have converted the acid into a related substance containing less bromine. Strong hydrobromic acid was boiled with the acid for 8 hours, and the original substance was recovered unaltered. Phosphoric pentabromide seemed to act on the substance, but the product was so uninviting that the work was not continued. Acetic anhydride, acetyl chloride, or benzoyl chloride in the Baumann-Schotten reaction either had no action, or produced far-reaching decompositions of the acid.

Action of Bromine and Water on the Tribromcarboxylketocyclopentene Ether of Oxalhydroxyacetic Acid

When a concentrated aqueous solution of the acid melting at 207° was mixed with bromine, and heated, a heavy, yellow precipitate was formed, which melted to a clear yellow oil. The reaction was accompanied by evolution of carbonic dioxide, the amount of which was determined by collection in a baric hydroxide solution, and weighing the baric carbonate formed:

I. 0.6687 gram acid gave 0.7531 gram $BaCO_3$.
II. 1.3800 grams acid gave 1.7068 grams $BaCO_3$.
III. 0.4984 gram acid gave 0.5916 gram $BaCO_3$.

	Calculated for 3 molecules of CO_2	Found I	II	III
CO_2	25.98	25.16	27.62	26.51

It is evident, therefore, that each molecule of the acid gave off three molecules of carbonic dioxide. Oxalic acid was detected in the aqueous liquid but in small quantity, as it left only an insignificant residue on evaporation. The yellow oil, which solidified on cooling to an orange-yellow crystalline product, was recrystallized from naphtha until it showed the constant melting point 97°–98°.[1] This substance was most conveniently prepared in quantity direct from the orthoquinone as follows: 200 grams of sodic hydroxide were dissolved in a liter of water, cooled to a few degrees above zero, and treated with 100 grams of tetrabromorthoquinone, which were added in small portions at a time with constant shaking. These are the conditions for making the acid melting at 174°, which gives this same bromine derivative. The dark solution with a brown precipitate was allowed to stand several hours to complete the reaction, and was then poured into a beaker containing about 300 cc. of strong hydrochloric acid, which was somewhat more than enough to neutralize the alkali. The mixture was allowed to stand overnight, as this made it easier to filter off the tetrabrompyrocatechin, and after this had been removed, the filtrate in a two-liter flask was treated with 5 cc. of liquid bromine, and shaken till it had been entirely absorbed. This treatment with liquid bromine was continued until a permanent red color in the solution indicated that an excess had been added, when the flask was heated on the steam bath for several hours. At the end of this time the solution with the oil below it was poured into a beaker and allowed to cool, when the oil solidified, and was easily removed. The yield of this crude product did not rise above 30 grams. The yellow crystalline solid was purified by pressing with filter paper to remove an oily impurity, followed by crystallization from naphtha, until it showed the constant melting point 97°–98°. It was dried *in vacuo* for analysis.

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[1] Different results were obtained with dilute bromine water or with pure bromine. They will be described later.

I. 0.2666 gram substance gave 0.0962 gram CO_2 and 0.0138 gram H_2O.

II. 0.3359 gram substance gave 0.1166 gram CO_2 and 0.0150 gram H_2O.

III. 0.2033 gram substance gave 0.4097 gram AgBr.

IV. 0.0810 gram substance gave 0.1637 gram AgBr.

	Calculated for $C_5HBr_7O_2$	Found I	II	III	IV
C	9.20	9.84	9.47		
H	0.15	0.58	0.50		
Br	85.90			85.78	86.00

The substance has been determined by the reactions discussed later to be a diketone, the heptabrommethyldiacetyl $CBr_3CHBrCOCOCBr_3$.

Properties.—It crystallizes from naphtha in brilliant yellow plates shaped like an arrow head and from alcohol in diamond-shaped scales, but a slight oily impurity is formed by the action of the alcohol on the substance. It melts at 97°–98°. It is easily soluble in alcohol, methyl alcohol, ether, benzene, carbonic tetrachloride, or glacial acetic acid; slightly soluble in naphtha; essentially insoluble in water. Naphtha is the best solvent for it. Fuming nitric acid, when boiling, dissolves it, and the compound seems to crystallize out unaltered, but analyses showed that it had lost between one and two per cent. of bromine. If boiled for several hours with nitric acid, complete decomposition takes place, as the solution leaves no residue on evaporation. Boiling with sulphuric acid diluted with its own volume of water gives bromoform, but in such small amount that only a very slight decomposition is indicated. Strangely enough, it is much less stable toward water than toward this dilute acid, as, if it is boiled with water for some time, it is decomposed completely into bromoform, hydrobromic acid, and oxalic acid. A solution of sodic hydroxide decomposes the diketone with the formation of bromoform. Cold sodic methylate dissolves it, and the solution gives a test for a bromide but none for an oxalate. The principal product melted at 80° and was colorless. Unfortunately we did not have time to study it. If the sodic methylate was hot, the diketone was decomposed, giving bromoform, sodic bromide and sodic oxalate. The behavior of the diketone with an aqueous solution of sodic carbonate will be described in detail later. Boiling with an aqueous solution of sodic acetate converted the diacetyl into bromoform, hydrobromic acid and oxalic acid. When boiled with water containing calcic carbonate a sharp odor like that of a brom ketone was observed, but only tarry products were obtained from which no definite compound could be isolated. The same odor was produced by boiling with water containing finely divided silver, and oxalic acid and bromide of silver were formed. When the diacetyl was shaken with a mixture of aqueous ammonic hydroxide and alcohol, a precipitate was formed, recognized as oxamide by its essential insolubility in all solvents but glacial acetic acid, its infusibility, and its decomposition by an alkali into ammonia and an oxalate. Analyses confirmed this inference. A benzene solution of the diketone treated with aniline gave a white precipitate consisting of pearly scales, which after crystallization from glacial acetic acid melted at 245°–246°; it was therefore oxanilide, which according to Gerhardt[1] melts at 245°. Boiling alkali converted it into aniline and an oxalate. As phenylhydrazine formed a large amount of its hydrobromide, when it acted on the diacetyl, we did not attempt to study its behavior further. Hydroxylamine hydrochloride had no apparent action on it. *o*-Phenylenediamine in benzene solution gave in time a grayish yellow precipitate, which did not melt below 275°, and was free from bromine. It was slightly soluble in the organic solvents except hot glacial acetic acid, and crystallized in very small prisms terminated by a basal plane. It contained 16.53 per cent. of nitrogen, and is therefore probably the *o*-phenyleneoxamide,[2] which contains 17.29 per cent. of nitrogen. Pyridine converted the diacetyl into a black tar containing a few colorless crystals. No action could be obtained with acetic anhydride, or acetyl chloride reinforced by sodic acetate, even when boiled for several hours, and the Baumann-Schotten process was also without action. Preliminary experiments on the reduction of the diacetyl led to no satisfactory result. Sulphurous acid apparently did not act, while zinc and acetic acid or aluminum amalgam seemed to give tars. Bromine in the cold did not seem to affect the diacetyl, and when heated with it in a sealed tube, tarry products were formed.

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[1] Ann. Chem. (Liebig), **60**, 308 (1846).

[2] R. Meyer, Seeliger: Ber. d. chem. Ges., **29**, 2641.

Decomposition of Heptabrommethyldiacetyl by Sodic Carbonate

When the diketone was allowed to stand several days with a solution of one gram of sodic carbonate in 10 grams of water, carbonic dioxide was given off, an oil collected at the bottom, and the water gave strong tests for bromide and oxalate; these seemed to be the only soluble products, as, after removing the oil, a portion of the solution was acidified with hydrochloric acid, and extracted with ether, to which it gave up nothing but a little oxalic acid. In addition to the oil, the bromide, and the oxalate there should be another product containing the fifth atom of carbon, but a careful search for formaldehyde, or formic acid, which we expected, failed to detect either, so that we are of the opinion that this atom of carbon was converted into carbonic dioxide, which escaped with that formed from the sodic carbonate; and this view is supported by the appearance of some carbonic dioxide when the diacetyl undergoes a similar decomposition on being heated to 100° with water.

The oil mentioned above was obtained in such small quantities that a determination of the boiling point in the usual way could not give a result definite enough to be of any value in identifying it. Accordingly we used the following method contrived by one of us (Fiske) for this purpose. The oil separated from the aqueous liquid was distilled with a few drops of water from a small side-neck test tube, when the boiling point was found to be 93°–94° with the barometer at 762 mm. The vapor pressure of water at that temperature is 599 mm.,[1] and subtracting this we obtain 163 mm. as the vapor pressure of the other liquid. As from its odor we suspected that our oil was bromoform, we next found the vapor pressure of bromoform at this temperature from the determinations given in the following table:

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[1] Landolt and Börnstein, 119 (1905).

Vapor Pressures of Bromoform

Temperature	Pressure
46°	14–15 mm.
50°.6	20.8 mm.
54°.6	26.24 mm.
61°.6	37.88 mm.
68°.2	54.46 mm.
150°.5	760 mm.
151°.2	760 mm.
120°.3	330 mm.

The last two observations are given by Thorpe,[1] the others by Kahlbaum.[2] From these data a curve was constructed (Fig. I), which showed that the vapor pressure at 93°–94° was between 162 and 164 mm., that is, as near to an exact agreement with our 163 mm. as the roughness of the method permits. The oil, which had distilled over with the water, was next dried by wiping with moist filter paper[3] and analyzed.

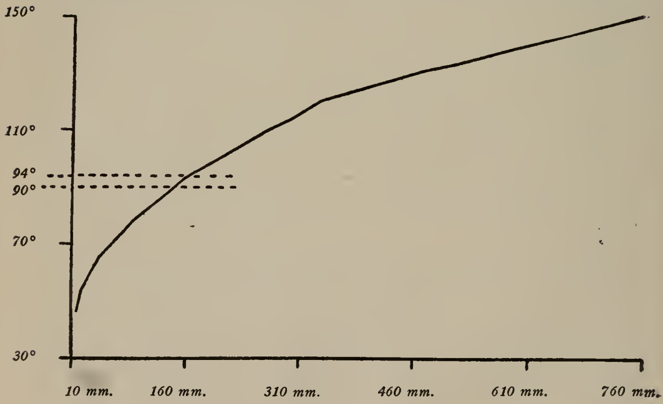

Fig. I

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[1] P. Chem. Soc., **37**, 201.

[2] Siedetemperature und Druck, 96.

[3] Jackson, Fiske: This Journal, **44**, 438 (1910).

I. 0.2943 gram substance gave 0.6560 gram AgBr.
II. 0.2391 gram substance gave 0.5339 gram AgBr.

	Calculated for $CHBr_3$	Found I	Found II
Br	94.86	94.86	94.99

There can be no doubt, therefore, that the substance is bromoform.

We also determined the amounts of the three decomposition products. For this purpose a weighed portion of the diacetyl was allowed to stand with a solution of sodic carbonate until it was completely decomposed. It was then distilled until the bromoform had passed over, when the residue was acidified with acetic acid, the oxalic acid determined by precipitation with calcic nitrate, and the bromide precipitated from the filtrate with argentic nitrate after acidification with nitric acid. An approximate idea of the amount of bromoform was obtained by weighing it after separation from the distilled water. To do this it was poured into a bulb, the bottom of which had been drawn out to a sealed capillary tube; after the oil had collected, the end of the capillary was broken, and the bromoform blown out through it, thus effecting a separation from all but a fraction of a drop of the water, which was then removed by wiping with moist filter paper.

I. 0.6040 gram substance gave 0.0487 gram CaO, 0.2319 gram AgBr and 0.3524 gram $CHBr_3$.

II. 0.5866 gram substance gave 0.0453 gram CaO, 0.1833 gram AgBr and 0.3182 gram $CHBr_3$.

	Calculated for $C_6HBr_7O_2$	Found I	Found II
$H_2C_2O_4$	13.78	12.96	12.41
Br	12.26	16.28	13.30
$2CHBr_3$	77.50	58.34	54.25

The percentages of oxalic acid found agree as closely as could be expected with that required by the formation of one molecule of oxalic acid. While the results for the bromine show great variations, they make it plain that only one atom of bromine was eliminated as sodic bromide. The variations are probably due to the decomposition of a larger or smaller portion of the bromoform. This would also interfere with the accuracy of the determination of the bromoform, but is insignificant compared with the losses in distilling, collecting, and, above all, in drying this substance by wiping. In our paper[1] on this method of drying we show that about one-third of the substance is usually lost, and, if that was the case here, our results are very near to the calculated percentage for two molecules of bromoform. But it is not necessary to apply this rather doubtful correction in order to use our results, for, as they stand, they are about 20 per cent. higher than 38.75, the percentage calculated for one molecule, and since all the experimental errors in our process tend to diminish the amount of bromoform found, our results, showing that much more than one molecule was formed, indicate that the actual quantity was two molecules.

Action of Water at 100° on the Diketone.—When the diketone was heated to 100° in a sealed tube with water for several days, a white crystalline substance was the principal product of the reaction, although small quantities of bromoform and carbonic dioxide and 17 to 19 per cent. of hydrobromic acid were also observed. The main product after recrystallization from alcohol showed the constant melting point 71°–72° and was dried *in vacuo* for analysis (Analyses I–II). What seemed to be the same compound was obtained from the mother liquors of the diketone in purifying that substance. It melted at 70°, but gave the same result on analysis (IV and V).

I. 0.1161 gram substance gave 0.2416 gram AgBr.
II. 0.1789 gram substance gave 0.3715 gram AgBr.
III. 0.1330 gram substance gave 0.2763 gram AgBr.
IV. 0.1143 gram substance gave 0.2387 gram AgBr.
V. 0.2279 gram substance gave 0.4736 gram AgBr.

	Found				
	I	II	III	IV	V
Br	88.53	88.37	88.39	88.88	88.43

Experiments are now in progress to settle the constitution of this substance. It crystallizes in bunches of long, thin, pale yellow needles, which turn slightly brownish on exposure to the air. It melts at 71°–72°. It is easily soluble in alcohol, methyl alcohol, ether, chloroform, tetrachloride of carbon, acetone, ethyl acetate, glacial acetic acid, or benzene, fairly soluble in ligroin, essentially insoluble in water. The best solvent for it is hot alcohol. The substance is tolerably stable, as standing for two days with cold alcohol left it unchanged, and the same was true of acetic anhydride in the cold. Analysis III was made with a specimen which had undergone this treatment. If boiled with acetic anhydride, an uncrystallizable oil was formed.

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[1] This Journal, **44**, 438 (1910).

Heptabrommethyldiacetyl Monomethyl Hemiacetal,

$CBr_3C(OH)(OCH_3)COCHBrCBr_3$

The diketone dissolved in absolute methyl alcohol was allowed to stand at ordinary temperatures for two days, and the solvent was then allowed to evaporate spontaneously, when colorless prisms were obtained. These were recrystallized from methyl alcohol until they showed the constant melting point 100°–101° when they were dried *in vacuo.*

I. 0.3053 gram substance gave 0.1178 gram CO_2 and 0.0265 gram H_2O.

II. 0.1436 gram substance gave 0.2746 gram AgBr.

III. 0.2177 gram substance gave 0.4160 gram AgBr.

	Calculated for $C_5HBr_7O_2CH_3OH$	Found		
		I	II	III
C	10.51	10.52		
H	0.73	0.97		
Br	81.75		81.21	81.32

Properties of Heptabrommethyldiacetyl Monomethyl Hemiacetal.—It crystallizes from methyl alcohol in colorless prisms, which melt at 100°–101°, and tend to turn brown when exposed to the air, especially if moist. It is easily soluble in alcohol, methyl alcohol, chloroform, tetrachloride of carbon, acetone, ethyl acetate, or benzene, less soluble in ligroin; essentially insoluble in water. When boiled with sulphuric acid diluted with its own volume of water, it was converted into an oil, and gave off an odor like camphor. It dissolved partially in strong nitric acid but apparently without decomposition, as the solution gave no test for bromine. Alcoholic ammonia formed ammonic bromide. Aniline gave an oil. Hydroxylamine hydrochloride, acetic anhydride, or acetyl chloride did not act upon it. A methyl alcohol solution boiled for some time with finely divided silver gave an oil which, on standing, deposited white crystals melting at about 70°, but we have not had time to study them.

Heptabrommethyldiacetyl Monoethyl Hemiacetal,

$CBr_3C(OH)(OC_2H_5)COCHBrCBr_3$

The diketone allowed to stand with alcohol for two days deposited large masses of colorless crystals, which were recrystallized from alcohol until they showed the constant melting point 93°–94°, when they were dried *in vacuo*.

I. 0.2257 gram substance gave 0.1016 gram CO_2 and 0.0255 gram H_2O.

II. 0.1661 gram substance gave 0.3129 gram AgBr.

III. 0.1849 gram substance gave 0.3464 gram AgBr.

	Calculated for $C_5HBr_7O_2.C_2H_5OH$	Found I	II	III
C	12.01	12.35		
H	1.00	1.25		
Br	80.11		80.17	79.75

Properties of Heptabrommethyldiacetyl Monoethyl Hemiacetal.—It crystallizes from hot alcohol in irregular masses of flat angular plates forming serrated ridges, which are white but easily turn brown when moistened with the solvent and exposed to the air. Specimens which had undergone this change were found on analysis to give amounts of bromine which were about 2 per cent. too low. It melts at 93°–94°. It was easily soluble in alcohol, methyl alcohol, ether, acetone, or ethyl acetate; soluble in benzene, chloroform, tetrachloride of carbon, or glacial acetic acid; slightly soluble in ligroin; essentially insoluble in water.

When a specimen of the ethyl hemiacetal was heated with a few cc. of water to 100° for several days, upon opening the tube a little carbonic dioxide escaped, and there was left an oil and an aqueous liquid. The oil smelled of bromoform, but after this had been allowed to evaporate, the residue was still oily, with a bitter ethereal odor, and contained a few crystals of the unaltered hemiacetal. These were removed, and the oil on distillation was found to boil between 183° and 193°, but owing to the small amount of substance no more accurate determination could be made. It is probably therefore the diethyl oxalic ester which boils at 186° according to Weger,[1] and can be formed by distillation from the monoethyl ester,[2] the secondary products being ethyl formic ester and carbonic dioxide. This inference was confirmed by a determination of the quantity of oxalic acid in the water solution, which amounted to less than 1 per cent. No formic acid could be detected in the products of the reaction, but much hydrobromic acid was formed.

Sodic carbonate in aqueous solution decomposed the hemiacetal in the same way that it did the diketone, but a quantitative study of this reaction gave less satisfactory results. The amount of bromoform was over 10 per cent. above that required by one molecule; the bromine agreed fairly with the amount for one atom, but the oxalic acid was only about half the percentage required by one molecule. This experiment therefore confirms the one tried with the diketone itself, the deficiency in oxalic acid being accounted for by the formation of oxalic ester.

Hydroxylamine hydrochloride or cold acetic anhydride had no action on the monoethyl hemiacetal; hot acetic anhydride converted it into an uncrystallizable oil. When the diketone was heated with alcohol a more deep-seated reaction took place than in the cold, giving tarry products with an odor like that of a brom ketone.

Action of other Alcohols on Heptabrommethyldiacetyl

When this diketone was allowed to stand with amyl alcohol for several days, and then freed from the alcohol by a blast of air, a yellow oil was obtained, which we did not succeed in bringing to crystallization. To our great surprise an analysis gave a percentage of bromine agreeing with that in the hemiacetal.

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[1] Ann. Chem. (Liebig), **221**, 87 (1884).

[2] Anschütz: Ber. d. chem. Ges., **16**, 2413 (1883).

0.2433 gram substance gave 0.4291 gram AgBr.

	Calculated for $C_5HBr_7O_2C_5H_{11}OH$	Found
Br	75.58	75.06

Similar treatment of the diketone with benzyl alcohol gave a solid product which crystallized from hot alcohol in large, colorless crystals showing the constant melting point 104°–105°, but the analyses proved the substance was not the expected hemiacetal, as we found C 22.58, H 1.90, Br 67.89, 68.29, 67.90, and $C_5HBr_7O_2C_7H_7OH$ requires C 18.92, H 1.16, Br 73.55. We have not succeeded in finding, for this substance, any formula which could be derived simply from those of its constituents, so that its nature must be left unexplained until more work can be done on it.

Action of Bromine on a Dilute Solution of the Tribromcarboxylketocyclopentene Ether of Oxalhydroxyacetic Acid

As already stated, bromine acting on a strong solution of the acid melting at 207° converts it into the heptabrommethyldiacetyl melting at 97°–98°, but if a dilute solution of the acid was treated with bromine in the cold, a precipitate was formed which was white instead of yellow, much less carbonic dioxide was given off, and a little of an oil was obtained, identified as bromoform by its smell and its vapor pressure when distilled with water according to the method already described. The colorless precipitate was crystallized from ligroin, until it showed the constant melting point 96°–97°. It is strange that this is so near to that of the diacetyl, 97°–98°. That it was a different substance is shown not only by the following analyses, but by its white color and behavior with sodic carbonate. The substance was dried *in vacuo*.

I. 0.2903 gram substance gave 0.1299 gram CO_2 and 0.0395 gram H_2O.

II. 0.2421 gram substance gave 0.1079 gram CO_2 and 0.0285 gram H_2O.

III. 0.2166 gram substance gave 0.4038 gram AgBr.

IV. 0.1899 gram substance gave 0.3536 gram AgBr.

	Calculated for $C_7H_5Br_7O_3$	Found I	II	III	IV
C	12.05	12.21	12.15		
H	0.72	1.17	1.31		
Br	80.35			79.34	79.21

These results agree fairly with those calculated for $CBr_3COCH(OCH_2CHO)CHBrCBr_3$, and as this substance would be expected from the method of preparation, we assign this constitution to it provisionally. Attention should also be drawn to the fact that this formula has essentially the same percentage composition as the heptabrommethyldiacetyl monoethyl hemiacetal $CBr_3C(OHOC_2H_5)COCHBrCBr_3$, as they differ only by 2 atoms of hydrogen. In many of their properties the two substances resemble each other, but this compound cannot be the hemiacetal, because no alcohol was used in its preparation, and also since it behaves in an entirely different way with sodic carbonate.

Properties of the Heptabromketosecondaryamyl Ether of Glycolaldehyde.—It crystallizes from alcohol in short, thick, white prisms, which show a tendency to turn brown on exposure to the air. It melts at 96°–97°. It is easily soluble in alcohol, methyl alcohol, or benzene, but each of these solvents converts it partially into a sticky liquid. Ligroin, in which it is less soluble, is the best solvent for it.

When this compound was allowed to stand with a solution of sodic carbonate, only a trace of bromoform was obtained, the product being a voluminous precipitate of white crystals, while bromide, but no oxalate, was detected in the aqueous liquid. The precipitate was recrystallized from ligroin, until it showed the constant melting point 71°–72°, when it was dried *in vacuo*.

I. 0.1550 gram substance gave 0.2758 gram AgBr.
II. 0.1303 gram substance gave 0.2322 gram AgBr.

	Calculated for $C_7H_6Br_6O_4$	Found I	II
Br	75.70	75.73	75.86

This compound, therefore, is formed by the replacement of one atom of bromine by hydroxyl in the preceding substance and its provisional formula is $CBr_3COCH(OCH_2CHO)$-$CH(OH)CBr_3$. It is unfortunate that the importance of these compounds was not appreciated until it was too late to settle their constitution definitely by further work.

Properties of the Hexabromketohydroxysecondaryamyl Ether of Glycolaldehyde.—It forms white crystals melting at 71°–72°, which are soluble in most of the organic solvents, except ligroin. In this it is soluble only when hot; insoluble in water.

When the dry acid melting at 207° was treated with dry bromine, no action could be detected, but on adding water the effervescence accompanying the formation of the diacetyl at once set in.

The Acid Melting at 121°

This substance was obtained occasionally from the benzene mother liquors left after the tribromcarboxylketocyclopentene ether of oxalhydroxyacetic acid (melting at 207°) had crystallized out, when they were allowed to stand in an open dish for some days. The new acid was deposited in large masses of colorless crystals, which were purified by recrystallization from benzene, until they showed the constant melting point 121°. They were dried *in vacuo*.

I. 0.3717 gram substance gave 0.5483 gram AgBr.
II. 0.2680 gram substance gave 0.3950 gram AgBr.

	Calculated for $C_{10}H_5Br_5O_7$	Found I	Found II
Br	62.81	62.76	62.72

It crystallizes from glacial acetic acid or benzene in white rhombic prisms, which melt at 121° with effervescence, leaving a residue which does not melt below 250°. The gas given off, which fumes in moist air and smells like hydrobromic acid, was identified as that body by passing it into water, when on addition of nitric acid and argentic nitrate it gave a yellowish white precipitate. It contains no carbonic dioxide, since it gave no precipitate with lime water. The acid is easily soluble in water, and in all the organic solvents except ligroin. Its aqueous solution set free carbonic dioxide from calcic carbonate. As the time at our disposal did not allow a fuller study of this substance it is not worth while to try to assign a formula and name to it.

The Acid Melting at 174.° Dibromhydroxycarboxylcyclopentene Orthodiether of Carboxyldihydroxyisocrotonlactone

This compound was prepared by dissolving 200 grams of sodic hydroxide in a liter of water, and adding to this solution, which had been cooled in an ice chest, 100 grams of tetrabromorthoquinone in small portions at a time with constant shaking. After standing for several hours to make sure that the reaction had run to an end, the liquid was poured into a large beaker containing 300 cc. of strong hydrochloric acid, which neutralized the alkali, and precipitated a sticky yellowish brown substance, and this after standing overnight was filtered out, and the filtrate extracted repeatedly with ether.[1] The residue left after the ether had evaporated spontaneously was not impregnated with oil, as in the preparation of the acid melting at 207°, and therefore was extracted with successive portions of hot benzene and then recrystallized either from this solvent, or from glacial acetic acid, until it showed the constant melting point 174°.

I. 0.2588 gram substance gave 0.2871 gram CO_2 and 0.0508 gram H_2O.

II. 0.2812 gram substance gave 0.3124 gram CO_2 and 0.0593 gram H_2O.

III. 0.2241 gram substance gave 0.1898 gram AgBr.

IV. 0.2594 gram substance gave 0.2194 gram AgBr.

	Calculated for $C_{11}H_6Br_2O_9$	Found			
		I	II	III	IV
C	29.64	30.26	30.28		
H	1.36	2.19	2.88		
Br	36.20			36.06	35.99

Properties of Dibromhydroxycarboxylcyclopentene Orthodiether of Carboxyldihydroxyisocrotonlactone.—It separates from ether in pale yellow, round grains, which are very pulverulent when dry. It melts at 174° with decomposition; and is easily soluble in water, alcohol, methyl alcohol, ether, acetone, glacial acetic acid, ethyl acetate, or benzene; slightly soluble in chloroform, or tetrachloride of carbon; essentially insoluble in naphtha. The best solvent for it is glacial acetic acid, in which it is much more soluble hot than cold. The aqueous solution gives an acid reaction with litmus paper, and decomposes carbonates with evolution of carbonic dioxide.

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[1] The extraction was most economically carried on in the apparatus invented by one of us (Fiske), THIS JOURNAL, 41, 510 (1909).

The basicity of the acid was determined by titration with a fifth-normal solution of potassic hydroxide, phenolphthalein being used as the indicator.

I. 0.1945 gram substance required 7.54 cc. of the solution.
II. 0.2793 gram substance required 10.35 cc.

	Calculated for $C_{11}H_3Br_2O_9K_3$	Found I	II
K	21.09	23.27	22.46

The acid is therefore tribasic, but we did not succeed in preparing salts of it in a state fit for analysis. Our attempt which approached most nearly to success consisted in treating a strong aqueous solution of the acid with baric carbonate, and, after warming to drive off the excess of carbonic dioxide, filtering and evaporating to dryness. The filtrate turned brown, as it evaporated, but in spite of this two determinations of barium were made, which gave 21.61 and 21.38 per cent. of Ba instead of 23.73, the amount in $BaH_4C_{11}Br_2O_9$. The water of crystallization also came out 1 per cent. below that required for one molecule. Attempts to avoid the decomposition of the salt by working in the cold gave discordant results, owing to the dissolved baric carbonate. An attempt to make the ammonium salt gave a brown solution containing ammonic bromide. A solution of the calcium salt made from the acid and calcic carbonate gave brown precipitates with argentic nitrate, mercurous nitrate, or plumbic acetate. When the acid melting at 174° was treated with bromine and water, it gave the heptabrommethyldiacetyl, $CBr_3CHBrCOCOCBr_3$, also obtained from the acid melting at 207°; in fact, our principal supply of this diketone was obtained from this acid. The amount of carbonic dioxide given off during the action of bromine and water on the acid was determined as follows:

I. 0.1945 gram substance yielded 0.2580 gram $BaCO_3$.
II. 0.2793 gram substance yielded 0.3943 gram $BaCO_3$.

	Calculated for 3 molecules of CO_2	Found	
		I	II
CO_2	29.80	29.63	31.53

It therefore also gives off three molecules of carbonic dioxide like the acid melting at 207°, under which the details of the method of determination will be found. The diketone was identified by its melting point, 97°–98°, its bright yellow color, and arrow-head crystals. When the action of bromine on a more dilute solution of the acid melting at 174° was tried, none of the colorless substance melting at 96°–97° was formed, which was obtained under the same conditions from the acid melting at 207°, but the product was the yellow diketone. The reactions also differed in the fact that no bromoform was produced in this case.

The Acid Melting at 217°

Tetrabromorthoquinone was shaken for 10 minutes with a normal solution of sodic hydroxide cooled to 6°. At the end of this time the green color, which appeared at first, had disappeared, and the liquid was acidified with hydrochloric acid, and after filtering out the precipitate of tetrabrompyrocatechin extracted with ether. Upon evaporating off the ether a crystalline solid impregnated with a yellow oil was obtained, which was pressed on a porous plate to remove the oil, and then crystallized from hot benzene until it showed the constant melting point 217°, when it was dried *in vacuo.*

I. 0.2011 gram substance gave 0.2525 gram AgBr.
II. 0.2288 gram substance gave 0.2895 gram AgBr.

	Calculated for $C_{10}H_6Br_4O_9$	Found	
		I	II
Br	54.23	53.43	53.81

Properties.—It crystallizes in shining yellowish white prisms, which melt at 217° with decomposition. It is easily soluble in all the common organic solvents except benzene and ligroin. In benzene it is slightly soluble in the cold, soluble when hot; in ligroin it is almost insoluble; soluble in water. Benzene is the best solvent for it. It has a strong acid reaction and its aqueous solution decomposes calcic carbonate.

The salts are far from stable, potassic carbonate, for example, giving a reddish solution with the acid, and the calcium salt turning brown when its solution is evaporated. In spite of this, however, we obtained a calcium determination which agrees well with the analyses for bromine given above.

The calcium salt was prepared by the action of a strong aqueous solution of the acid on an excess of calcic carbonate; the aqueous solution was boiled to drive off carbonic dioxide, filtered, and the filtrate evaporated to dryness.

I. 0.2428 gram of the air-dried salt lost 0.0361 gram on heating to 110°.

II. 0.2074 gram substance gave 0.0467 gram $CaSO_4$

	Calculated for $C_{10}H_4Br_4O_9Ca.6H_2O$	Found
H_2O	14.68	14.86
	Calculated for $C_{10}H_4Br_4O_9Ca$	Found
Ca	6.37	6.62

Although this determination agrees with our analyses for bromine, we feel that more experimental work is necessary before the formula given above can be considered definitely established.

The solution of the calcium salt gave a black precipitate with argentic nitrate, or mercurous nitrate, a dark brown precipitate with plumbic acetate, or ferric chloride, a yellow precipitate with baric chloride, no precipitate with mercuric chloride, or cobaltous nitrate. We are unable to determine whether the colors of these precipitates belonged to the salts, or were caused by the decomposition observed during the boiling off of the carbonic dioxide in making the calcium salt.

When treated with bromine and water, the acid melting at 217° did not give the heptabrommethyldiacetyl melting at 97°–98° obtained from the acids melting at 207° and 174°. Instead of this, white needles were formed melting at 156°, and showing a tendency to turn brown on exposure to the air Unfortunately the time at our disposal did not permit us to make a further study of this promising substance, or of the other properties of the acid melting at 217°.

The Oily Product

By the action of the weaker solutions of sodic hydroxide on tetrabromorthoquinone an oily product was obtained in addition to the solid acid melting at 207° or 217°, but none of this was formed with the stronger lye which gave the acid melting at 174°. In the introduction we have shown that certain inferences in regard to the nature of the oil can be drawn from our quantitative experiments, the details of which follow. A fifth-normal solution of potassic[1] hydroxide was used, therefore much more dilute than those which had yielded our definite acids. The amount of alkali used was determined by mixing an excess of it with a weighed quantity of powdered tetrabromorthoquinone, and allowing the mixture to stand in a corked flask until the reaction was complete, when the excess of alkali was determined by titration with one-fifth normal hydrochloric acid, phenolphthalein being used as the indicator. The carbonic dioxide formed was collected in a solution of baric hydroxide, the whole being set free by a large excess of hydrochloric acid and heat. The bromine removed was determined by another experiment, in which the quinone was decomposed by potassic hydroxide free from halogen, and the solution precipitated with argentic nitrate after acidification with nitric acid. The argentic bromide was freed from organic matter by treatment with a large amount of alcohol, followed by hot nitric acid, and finally by washing again with water and alcohol.

I. 0.3482 gram $C_6Br_4O_2$ used 14.12 cc. KOH solution and gave 0.0607 gram $BaCO_3$.

II. 0.4538 gram $C_6Br_4O_2$ used 17.52 cc. KOH solution and gave 0.0554 gram $BaCO_3$.

III. 0.4549 gram $C_6Br_4O_2$ used 17.78 cc. KOH solution and gave 0.0561 gram $BaCO_3$.

IV. 0.4234 gram $C_6Br_4O_2$ gave 0.3841 gram AgBr.

V. 0.3866 gram $C_6Br_4O_2$ gave 0.3504 gram AgBr.

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[1] Potassic hydroxide apparently acts like sodic hydroxide.

	Found for each molecule $C_6Br_4O_2$				
	I	II	III	IV	V
KOH	192.9	183.7	186.0		
CO_2	16.47	11.53	11.65		
KBr				243.7	243.5

The results are given in units of molecular weight, and agree even more closely than we expected.

THE BEHAVIOR OF TETRABROMORTHOQUINONE WITH ALKALINE REAGENTS OTHER THAN SODIC HYDROXIDE

As stated earlier in this paper an aqueous solution of sodic hydroxide converted the tetrabromorthoquinone into a green substance which disappeared after the reagents had been shaken together for 10 or more minutes. The aqueous liquid thus obtained gave, on acidification, tetrabrompyrocatechin, and on extracting the filtrate from this with ether one or more of the acids already described. In the hope of tracing the limits of the reaction experiments were tried in which the nature of the alkaline substance was varied; and these showed that potassic hydroxide or ammonic hydroxide gave results apparently similar in every way to those obtained with sodic hydroxide, and therefore they were not studied in detail. A half-normal solution of baric hydroxide after standing for several days in the cold gave a green product, which at the end of 10 days had changed into yellowish feathery crystals showing no test for a carbonate. When these were washed with water, a solution with the strong purple color of sodic bromanilate was formed, and the solid became tarry. The filtrate from the crystals yielded on acidification no precipitate of tetrabrompyrocatechin, but this was to be expected, for a special experiment showed that the pale yellow barium salt of tetrabrompyrocatechin is insoluble. The acidified filtrate gave up to ether a yellow acid melting at 202°, when not perfectly pure, and therefore undoubtedly the acid melting at 207°. Plumbic hydroxide had no perceptible action on tetrabromorthoquinone.

A normal solution of sodic carbonate acted on tetrabromorthoquinone in the same way as sodic hydroxide, except that the solution was redder, the precipitate on acidification scanty and more tarry, and bromanilic acid was detected in addition to the acid melting at 217°. A normal solution of acid sodic carbonate in the cold gave none of the green compound but a chocolate-brown solid and much bromanilic acid, whereas, if the aqueous solution acted on a solution of the quinone in benzene, a greenish precipitate was formed and the solution (which was not colored by bromanilic acid) upon treatment with bromine and water gave colorless needles melting at 94°–95°, when not perfectly pure, and which were therefore probably the heptabromketosecondaryamyl ether of glycolaldehyde, which is colorless and melts at 96°–97°. The formation of this ether would indicate that the acid melting at 207° had been formed.

The effect of heat on the reaction was also studied. If a fifth-normal sodic hydroxide solution was warmed on the water bath with tetrabromorthoquinone for two minutes, no green product was formed, the red quinone being directly converted into a chocolate-brown substance, which after an hour on the steam bath had become dull red. Upon washing this solid with alcohol the red ether $C_6Br_4O_2C_6Br_2O_2$ was obtained in quantities of about 1 gram from five of the quinone. The appearance of the ether can be explained on the supposition that the boiling was not long continued enough to decompose it completely. The dark-colored solutions contained the other products of the reaction, of which we can give no account except that we did not succeed in detecting tetrabrompyrocatechin or bromanilic acid in them. The red ether $C_6Br_4O_2C_6Br_2O_2$ was also obtained by boiling the quinone with a solution of sodic carbonate, or of baric hydroxide, but the presence of the alkaline reagent is not necessary for the formation of the ether, as, when the tetrabromorthoquinone was boiled with water alone for half an hour, about one-fifth of it was converted into this ether. This result confirms the similar observation of Porter and one of us.[1] The same change seemed to take place very slowly in the cold.

In order to determine the source of the bromanilic acid observed in several of these experiments we studied the behavior of tetrabrompyrocatechin and of the hexabromorthoquinopyrocatechin ether with sodic hydroxide. By the action for 5 hours of a boiling twice-normal solution of sodic hydroxide a considerable amount of tetrabrompyrocatechin was converted into bromanilic acid, recognized by the deep purple color of its sodium salt; but in the cold the reaction did not take place even with this concentrated solution, and with more dilute alkaline solutions bromanilic acid could not be obtained even at the boiling point.

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[1] This Journal, **31**, 119 (1904); also **38**, 173 (1907).

The red ether $C_6Br_4O_2C_6Br_2O_2$, after standing in the cold for two days with a twice-normal solution of sodic hydroxide, gave a quantity of the black precipitate observed by Koch and one of us,[1] which was identified as sodic bromanilate, while some of it colored the solution purple-red. Acidification of the liquid gave a copious precipitate of tetrabrompyrocatechin, but none of our acids could be obtained from the filtrate, which gave up to ether nothing but a little bromanilic acid.

Cambridge, September 19, 1913

THE VISCOSITY OF UNDERCOOLED WATER AS MEASURED IN A NEW VISCOSIMETER

By George F. White and Ralph H. Twining

While there is at hand[2] a great variety of information concerning the change of many properties of substances in the region of their melting point, very little attention has been devoted to a study of the viscosity changes. The discontinuity of the viscosity curves of a few crystalline liquids at their melting point has been indicated by the work of Schenck,[3] and further investigation along this line should furnish results of considerable value. Tammann[4] regarded viscosity as an important criterion of the passage of a liquid into the crystalline condition, but observed that there is no "break" in the viscosity curves of liquids passing into the amorphous state. Amorphous substances could be considered as undercooled liquids. His investigations were not carried out at the melting point, but far below this temperature, where the viscosity of the undercooled liquid is enormously high and where there is a maximum in the number of nuclei which appear in a definite interval of time. At these temperatures no irregularities in the viscosity curves were observed.

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[1] This Journal, **26**, 10 (1901).

[2] Very recently [Gazz. chim. ital., **43**, II, 281 (1913)], Nasini and Bresciani have undertaken an investigation on the discontinuity phenomena at the melting point. This will be referred to in a later article.

[3] Z. physik. Chem., **27**, 167 (1898).

[4] *Ibid.*, **28**, 17 (1899).

The change in the rate of crystallization of a liquid on undercooling has been ascribed to many causes. Different investigators have stated that it is due to differences in the disposition of the crystals in their formation, to impurities in the liquid, to slow conduction of heat from the surface of crystallization, and may be influenced by the shape of the containing vessel. Wilson[1] considered the older explanations for the increase in velocity of solidification of undercooled liquids to a maximum as the temperature was lowered to be very unsatisfactory or incomplete. He supposed that it was a function of the viscosity, and deduced the relation $v = Ct/\eta$ where v is the velocity of crystallization, C a constant dependent on the nature of the liquid, t the degrees of undercooling, and η the viscosity. The temperature of the liquid in some cases was reduced to that at the surface of crystallization, which was at a higher temperature because of the latent heat of solidification. The velocities of crystallization as calculated agreed very well with those observed, and Wilson's assumption of a fundamental relation between viscosity and crystallization was well founded. His viscosity measurements were made by use of an Ostwald viscosimeter, and with more exact methods there is a possibility of developing a more rigid relationship.

In this preliminary paper there is presented a method for the measurement of the viscosity of liquids which eliminates many of the possibilities of error known up to this time, has practical application to the exceptionally viscous undercooled liquids and overcomes the difficulties attendant on working with them. After the collection of some necessary data on this subject, a study of the relation between the viscosity and crystallization velocity will be made, both for pure liquids and for solutions.

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[1] Phil Mag., [5] **50**, 238 (1900).

The extent to which a liquid may be undercooled depends largely on its power of spontaneous crystallization, and this power is peculiarly sensitive to conditions not fully understood. As Tammann[1] has pointed out, there is a change in this property with every recrystallization of betol. Admixture of substances of varying composition shows a very different influence. Thus betol could be undercooled about 20° with the addition of 0.5 per cent. naphthalene or 0.1 per cent. salicylic acid without the appearance of any nuclei within two minutes' exposure at that temperature. On the other hand, crystallization commenced above this temperature with an admixture of 0.1 per cent. succinic acid or 5 per cent. benzamide. Insoluble substances were shown to have a great effect. In one experiment at 30° in pure betol there appeared one nucleus in two minutes, whereas no crystals were observed in a mixture of betol and 0.5 per cent. powdered glass in the same time even on cooling to —10°.

Tammann proved that the volume of liquid has considerable influence on the number of nuclei formed, but, as would be expected, there was little effect on the temperature at which crystallization commenced. The intensity of light and the magnetic field were further shown to produce no change in the phenomena of crystallization.

Tammann studied the properties of about 140 undercooled liquids and found that these could be grouped roughly into four clases according to their power to be undercooled. In the first class he placed those substances which, in passing from the fusion bath, kept 10° above the melting point, to the undercooling bath crystallized practically instantaneously. In the fourth class were those substances which could be cooled through the region where there is a maximum in the number of nuclei, and correspondingly in crystallization velocity, without the appearance of any crystallization, to a temperature where the velocity is low. No rigid rules could be adopted concerning the relation of the property of undercooling to the nature of the substance. Hydrocarbons, alcohols, aliphatic acids and dicarboxyl acids in general may be undercooled little or not at all. Halogen and nitro derivatives of the hydrocarbons, polyatomic alcohols, hydroxy acids, aldehyde alcohols, keto acids, alkaloids and glucosides may be more or less undercooled.

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[1] Z. physik. Chem., **25**, 439 (1898).

Water may be undercooled very little, especially if kept in motion, without spontaneously crystallizing. We have, however, commenced our study of the viscosity of undercooled liquids with this substance in order to test the accuracy of the apparatus used, and because we consider it particularly important to establish the exact viscosity-temperature curve in the region of its melting point.

EXPERIMENTAL

Probably the most convenient form of an accurate viscosimeter which depends for the measurement of viscosity only on the physical constants of the instrument itself, and eliminates the well-known errors of the Ostwald type, is that of Bingham and White.[1] In experimenting with undercooled liquids, however, especially those which, like water, expand on solidifying and accordingly are apt to break the viscosimeter, an instrument should be used which can be most quickly constructed and calibrated. That devised by one of us[2] was utilized in a modified form in the present work. It lessens the possibility of introducing glass powder, dust, or other extraneous matter into the liquid. It can be made and calibrated in a few hours, and its accuracy will be shown by comparison with the results of others.

The Poisseuille formula

$$\eta = \frac{\pi r^4 pt}{8vl} - \frac{vd}{8\pi tl}$$

was used for the calculation of the viscosity data. η is the viscosity, r the radius and l the length of the capillary tube, d the density of the liquid, v the volume of liquid passing through the capillary, p the pressure, and t the time of flow.

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[1] Z. physik. Chem., **80**, 670 (1912).

[2] Biochem. Z., **37**, 482 (1911).

The viscosimeter is shown in Fig. I, and was thus constructed in order to measure the viscosity of a liquid, through great ranges in this property, in one and the same instrument. In working with water from 25° down to 0° C., the total volume of liquid in the viscosimeter was that between the marks *J* and *T*, and at each temperature the liquid was forced down to the mark *J*, whereby it overflowed into the trap at *T*. The volume *v*, which is that amount of liquid passing through the capillary in the time *t*, was that between the marks *A* and *D*, this volume being determined before fusing the capillary tube onto the two limbs by taking the weight of water filling this volume and reducing it to standard conditions. Volume *AD* was found to be 7.3430 cc. Viscosity determinations were always made in duplicate by taking first the time of descent of the liquid from *A* to *D* and, second, the time of ascent from *D* to *A* with the pressure reversed. This procedure[1] avoids determining the volume of the right limb and its pressure correction, as was necessary in the original form of the instrument.[2] The viscosimeter was then standardized with water at 25°.

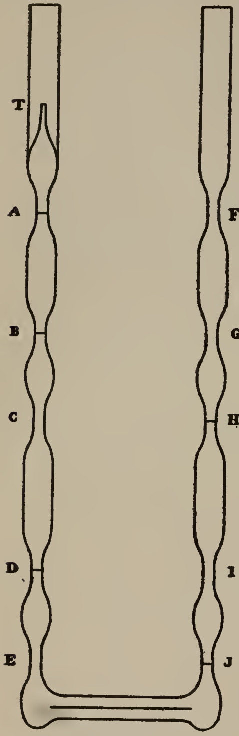

Fig. 1

$v/8\pi l$ was calculated from the known value of *v*, and an approximate value of *l* (8.3 cm.). Since this kinetic energy correction is very small, no error was introduced by a comparatively large deviation in the value of l. Taking Thorpe and Rodger's[1] value of η at 25° (0.00895), and determining p and t, from the mean of the results of four determinations the constant $\pi r^4/8l$ was calculated to be 1202×10^9. (The approximate diameter of the capillary was 0.1 mm.)

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[1] Cf. Bingham and White: Z. physik. Chem., **80**, 670 (1912).

[2] *Loc. cit.*

The viscosimeter was made as nearly symmetrical as possible, but as the bulbs horizontally opposite each other in the two limbs under any conditions would differ slightly in volume and in height above the capillary tube, and also the volume of TA might differ from that of IJ, the pressure as read in the manometer did not represent the true pressure on the liquid during its passage through the capillary. The correction of the pressure, caused by the difference in height of the center of gravity of the liquid in the volumes AD and FI, is the same, though opposite in sign, according to whether the reading is taken when the liquid descends or rises in AD. Since pt is a constant, this correction may be readily calculated.

At 25°, under a pressure of about 130 cm. of water at 20°, it took about 415 seconds for the volume AD of water to pass through the capillary. At 0° under the same conditions, the time was approximately 815 seconds. Since the viscosity increases very considerably below this temperature, the time for any one determination would correspondingly increase. The time for the determination of the viscosity of an undercooled liquid should be as brief as is consistent with a low kinetic energy correction, so that it may be completed before any possible crystallization. For temperatures below 0°, therefore, the volume v was AB (2.8080 cc.), and the viscosimeter was filled between the mark H and the top of the trap T. The time of measurement, that is, the time required for the liquid to pass up or down between A and B, was reduced to about 315 seconds at 0° and the above pressure. That concordant results were obtained by using the different volumes is proven by the fact that $\pi r^4/8l$ calculated from determinations with volume AB (η being taken from data obtained by the use of volume AD) gave as a result 1201×10^9, whereas the same value determined at 25° with volume AD gave 1202×10^9.

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[1] Phil. Trans. Lond., (A) **185**, 449 (1894).

Of course the correction of the pressure was determined anew for the different "working volume" *HT*.

By the above principle of varying volumes, liquids of very different viscosities can be used in the same instrument. r^4/l being determined, the chance of error in standardizing an instrument with a shorter capillary tube by means of a liquid of high viscosity is avoided. With liquids of the ordinary viscosity it is necessary to use only one as a standard, and the careful measurement of the viscosity of water at temperatures from 0° to 100° by many investigators gives this substance the preference. A viscosimeter, capable of wider application than the one constructed, could be made having three values for v, possibly 1 cc., 2 cc., and 7 cc., if a capillary tube of the dimensions described in this article were used. Three "working volumes" would be required for such an instrument, with six bulbs in each limb, and four etchings on the left and three on the right limb. By giving the bulbs an elliptical shape the viscosimeter could be much shortened.

The arrangement of the entire apparatus, manometer, air reservoir, pressure regulator, bath and stirrer, has been previously illustrated and described.[1] For standardizing the viscosimeter at 25°.00 (±0°.008), the bath was heated by an electric globe with a toluene regulator. For temperatures below 0° the viscosimeter was immersed in ice and sodium chloride mixtures contained in a large glass jar and well stirred.

The thermometer was calibrated and standardized at the Bureau of Standards, Washington, D. C., and read from —30° to +20° C. It was graduated in tenths of a degree. For calibration, a Reichsanstalt thermometer reading directly to hundredths of a degree was used.

The time was read by a stop-watch reading directly to 0.2 second.

Great care was exercised to obtain a sample of water free from dust, grease and dissolved matter. Ordinary distilled water was distilled once from a chromic acid solution, and finally redistilled from a barium hydroxide solution. It was preserved in Jena glass vessels which had been washed out with hydrochloric acid and the above redistilled water.

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[1] Biochem. Z, **37**, 484 (1911).

Table I

	Temp.	Viscosity	Av.
U	20°.00	0.01001	0.01003
D	20°.00	0.01004	
U	15°.00	0.01138	0.01139
D	15°.00	0.01140	
U	10°.00	0.01307	0.01307
D	10°.00	0.01306	
U	5°.00	0.01522	0.01523
D	5°.00	0.01523	
U	0°.00	0.01798	0.01798
D	0°.00	0.01798	
U	— 2°.10	0.01932	0.01930
D	— 2°.10	0.01928	
U	— 4°.70	0.02124	0.02121
D	— 4°.70	0.02117	
U	— 6°.20	0.02252	0.02250
D	— 6°.20	0.02247	
U	— 7°.23	0.02343	0.02341
D	— 7°.23	0.02338	
U	— 8°.48	0.02455	0.02458
D	— 8°.48	0.02461	
U	— 9°.30	0.02552	0.02549
D	— 9°.30	0.02546	

The viscosimeter was thoroughly cleaned by the use of fuming nitric acid. The acid was washed out with water and in some preliminary experiments this washing was followed by redistilled alcohol and redistilled ether. A current of warm air filtered through cotton wool was then drawn through the instrument to remove all the ether. By this treatment, however, water could not be undercooled in the viscosimeter below —6° without crystallizing. This was very probably occasioned by dust particles still present in the filtered air which passed through or to some minute quantity of non-volatile substance dissolved in the ether. To avoid drying with air and the use of ether, after washing with nitric acid

Table II

Temp.	Goodwin and Mailey	Poisseuille	Sprung	Slotte	Thorpe and Rodger	Hosking	Bingham and White	White and Twining
0°	0.01797	0.01716	0.01778	0.01808	0.01780	0.01793	0.01797	0.01798
5°	.....	0.01515	0.01510	0.01524	0.01512	0.01522	0.01525	0.01523
10°	.....	0.01309	0.01301	0.01314	0.01305	0.01311	0.01301	0.01307
15°	.....	0.01146	0.01135	0.01144	0.01137	0.01142	0.01138	0.01139
20°	.....	0.01008	0.01003	0.01008	0.01005	0.01006	0.01006	0.01003

and water, alcohol was drawn in and then completely removed by many washings with the purest water. Hereby no air at all was sucked through the capillary tube. The water could now be undercooled to —9.30°. One viscosimeter was shattered by crystallization of the liquid contained in it, but a second instrument was made, by use of which the results in this article were in general obtained, which withstood repeatedly the solidification.

Table I gives results obtained with water from 20° to —9.30°, the viscosities being expressed in C. G. S. units. U and D in the first column signify whether the readings were taken as the liquid was passing up or down in the calibrated limb. The viscosity from 20° to 0° was determined by use of the larger volume *AD*, and from 0° to —9.30°, by the smaller volume *AB*.

In Table II a comparison of the results of various observers with ours is made.[1]

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ON THE PINACOL-PINACOLIN REARRANGEMENT

THE PREPARATION OF BENZOYLFORMIC ACID[2] AND SOME OF ITS DERIVATIVES

[FOURTH[3] COMMUNICATION ON THE PINACOL-PINACOLIN REARRANGEMENT]

By S. F. Acree

(This work was made possible by a grant from the Carnegie Institution of Washington.)

In the preparation of various symmetrical and unsymmetrical pinacols the choice of cheap starting materials is limited. It seemed desirable, therefore, to attempt the easy preparation of benzoylformic ester and its homologues in order to convert

[1] The results of most of the observers were taken from tables in Landolt-Börnstein's Physikalisch-Chemische Tabellen; those of Bingham and White from Z. physik. Chem., **80**, 685 (1912).

[2] This work was done in 1904–05. Other investigations took our attention away from the pinacol-pinacolin rearrangement, which we are now studying again.

[3] This Journal, **29**, 588; **33**, 180. Ber. d. chem. Ges., **37**, 2753.

these first into the symmetrical and unsymmetrical dialkylglycollic esters by the use of the Grignard reagent:

$$\mathrm{C_6H_5COCOOC_2H_5 + C_7H_7MgBr \longrightarrow C_6H_5(C_7H_7)C(OH)COOC_2H_5} \quad (1)$$

or into the corresponding orthodiketones:

$$\mathrm{C_6H_5COCOOC_2H_5 + C_7H_7MgBr \longrightarrow C_6H_5COCOC_7H_7} \quad (2)$$

It was found that Reaction (1) takes place very easily. We had already[1] shown that the mono- and dialkylglycollic esters react very readily with the Grignard reagent and give pinacols in excellent yield, and we should now, therefore, be able to prepare unsymmetrical pinacols very easily:

$$\mathrm{C_6H_5(C_7H_7)C(OH)COOC_2H_5 + 2CH_3MgI \longrightarrow C_6H_5(C_7H_7)C(OH)C(OH)(CH_3)_2} \quad (3)$$

A few years before this work was begun we had shown that weak oxidizing agents, such as bromine in chloroform, and potassium permanganate oxidize the secondary alcohols of this series of derivatives fairly readily into the corresponding diketones:

$$\mathrm{C_6H_5COCH(OH)C_6H_5 + O(Br_2) \longrightarrow C_6H_5COCOC_6H_5 + H_2O(2HBr)}$$

and the thought suggested itself that mandelic acid should be oxidized to benzoylformic acid in the same way:

$$\mathrm{C_6H_5CH(OH)COOH \longrightarrow C_6H_5.\underset{\swarrow\searrow}{C}.COOH + O + H_2O\ (or\ 2OH) \longrightarrow C_6H_5COCOOH + H_2O}$$

The brilliant work of Nef,[2] Evans[3] and others on this subject of oxidation and reduction encouraged us all the more, and it seems that Nef's theory of bivalent carbon offers the best explanation of such ready oxidations, as is seen in the above equations.

The benzoylformic acid is formed very readily, in excellent yields, by the interaction of mandelic acid and potassium permanganate in cold dilute solutions. The ester and the benzoylformyl chloride are readily formed from the acid. We have undertaken further work along these lines, especially with lactic acid.

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[1] Ber. d. chem. Ges., **37**, 2761, 2763.

[2] See the literature on this subject in Ann. Chem. (Liebig) and THIS JOURNAL.

[3] J. Am. Chem. Soc., **35**, 1770, and earlier papers.

EXPERIMENTAL

The Preparation of Benzoylformic Acid, $C_6H_5COCOOH$, from Mandelic Acid.—Several different methods were tried, some of the details of which are given. The best results are obtained by rapid work. In one experiment, 100 grams of mandelic acid, neutralized with sodium hydroxide in one liter of water, was cooled with ice and treated slowly, during the course of 2 to 3 hours, with about 70 grams of potassium permanganate in as little water as possible. Alcohol was added to reduce the permanganate; the manganese dioxide was then filtered off and the solution acidified. About 20 grams of benzoic acid precipitated out and was removed by filtration. The filtrate was made neutral with alkali and evaporated to a small volume under 70 mm. pressure, acidified with sulphuric acid and extracted several times with ether, which was dried and distilled from the benzoylformic acid. The semisolid mass was mixed with carbon disulphide to dissolve the benzoic acid, well cooled and filtered. About 75 grams of the snow-white acid was thus obtained. When crystallized once more from carbon disulphide it melted at 63°–64°, and 0.1547 gram required 10.50 cc. 0.1 N potassium hydroxide instead of the theoretical volume, 10.31 cc.

In another similar experiment, in which the oxidation required four days, only 40 grams of benzoylformic acid was obtained. The oxidation must evidently be done rapidly, to prevent the oxidation of the benzoylformic acid to benzoic acid.

In another experiment, 30 grams of mandelic acid was neutralized with sodium hydroxide and oxidized with 20 grams of potassium permanganate. After having been treated with alcohol and filtered, the solution was made neutral and, from necessity, allowed to stand overnight. The next day it was acidified and extracted several times with ether, which was dried and distilled. The residue of benzoylformic acid was treated twice with carbon disulphide to remove the benzoic acid, dissolved in ether and dried with calcium chloride. When the ether was distilled off, there remained 27 grams of the liquid acid. This was then dissolved in 145 grams of absolute alcohol containing 7 grams of hydrogen chloride and heated 3 hours under a return condenser. When the alcoholic solution of the ester was poured into water, extracted with ether, dried and distilled *in vacuo*, only 15 grams of ethyl benzoylformate was obtained.

In another experiment, 50 grams of mandelic acid was oxidized with 35 grams of potassium permanganate, and the solution treated with alcohol and allowed to stand overnight. After the manganese dioxide was filtered off and the solution acidified, the benzoylformic acid was removed by repeated extraction with ether. The ethereal extract was dried and evaporated and an excess of alcoholic potash was added to precipitate the acid in the form of its potassium salt, of which 80 grams were obtained. The aqueous solution of this salt was acidified and extracted with ether. When the ether had been evaporated the liquid acid was dissolved in 330 grams of absolute alcohol containing 100 grams of hydrogen chloride and the mixture was boiled several hours. When the ester was isolated as usual, 45 grams were obtained and this was purified as follows: We converted 100 grams of sodium carbonate into sodium bisulphite in 200 cc. of water, and this was thoroughly shaken with the ester. The precipitate of the sodium bisulphite compound was filtered and washed with alcohol to remove any ethyl benzoate. The filtrate also gave another precipitate when the wash alcohol was added, and this second precipitate was washed with alcohol. The two precipitates were suspended in 300 cc. of water and decomposed with hydrochloric acid at an elevated temperature, the ester precipitating out. When this was extracted with ether, dried and distilled, 35 grams of pure ester, boiling at 265° under 766 mm., was obtained, together with about 9 grams of crude ester. The ester boils at 125° under 9 mm., gives the characteristic color test with concentrated sulphuric acid and thiophene in benzene and yields the sodium bisulphite compound when shaken with a 40 per cent. solution of sodium bisulphite. Some of the ester was made from the pure acid and analyzed.

0.1298 gram substance gave 0.3191 gram CO_2 and 0.0690 gram H_2O.

	Calculated for $C_{10}H_{10}O_3$	Found
C	67.38	67.05
H	5.67	5.91

Benzoylformyl Chloride, $C_6H_5COCOCl$.—When 10 grams of benzoylformic acid was boiled with a slight excess of thionyl chloride, $SOCl_2$, at 100°, we obtained only benzoyl chloride. The benzoylformyl chloride had apparently decomposed at some stage in the operations, with the loss of carbon monoxide:

$$C_6H_5COCOCl \longrightarrow C_6H_5COCl + CO$$

But by warming the same amounts at about 40° and fractionating the mixture under 9 mm., we got a small quantity of benzoyl chloride in the first fraction and then 6 grams of benzoylformyl chloride, which boiled at 125° under 9 mm. This acid chloride has an odor resembling that of benzoyl chloride. When treated with absolute alcohol, warmed and distilled, the acid chloride yielded the pure ester, which boiled at 125° under 9 mm. This ester gave the characteristic color tests and sodium bisulphite compound mentioned above. The ester was analyzed.

Analysis:

0.1571 gram of the substance gave 0.3858 gram CO_2 and 0.0861 gram H_2O.

	Calculated for $C_{10}H_{10}O_3$	Found
C	67.38	66.98
H	5.67	6.08

On the Action of Three Molecules of Phenylmagnesium Bromide on Ethyl Benzoylformate: Benzpinacol.—Fifteen grams of bromobenzene and 3 grams of magnesium were boiled 1 hour in 50 cc. of absolute ether, and 5 grams of the ester in 25 cc. of dry ether was added slowly. As each drop of the solution of the ester touched the solution of the Grignard reagent a white precipitate formed which dissolved when the solution was shaken. The mixture was boiled 2 hours, cooled and added to cold, dilute sulphuric acid. The ethereal layer was dried with calcium chloride and distilled. When the benzpinacol began to precipitate, 50 cc. of absolute alcohol was added and the remainder of the ether was removed by distillation. The alcoholic solution was cooled to —10° and filtered from benzpinacol, which weighed 8.2 grams and melted at 186°–187°. The filtrate gave more of the crude benzpinacol.

Analysis:

0.1420 gram substance gave 0.4438 gram CO_2 and 0.0819 gram H_2O.

	Calculated for $C_{26}H_{22}O_2$	Found
C	85.20	85.24
H	6.07	6.41

On the Action of Equimolecular Quantities of Phenylmagnesium Bromide and Ethyl Benzoylformate: Ethyl Benzilate.— In another article[1] it was shown that when an ethereal solution of the Grignard reagent is *added to* an ethereal solution of benzil, only one of the two carbonyl groups is attached and phenylbenzoin is formed:

$$C_6H_5COCOC_6H_5 + C_6H_5MgBr \longrightarrow (C_6H_5)_2C(OH)COC_6H_5$$

Work with the benzoylformic ester offers the same possibilities and it is purely a question of experiment to learn whether the carbonyl adjacent to the phenyl group or that in the ester group (or both) adds the Grignard reagent and forms ethyl benzilate or benzil. The reactions are found in the theoretical part in Equations (1) and (2).

The experiments show that ethyl benzilate is formed in excellent yield. Ten grams of bromobenzene and 2 grams of magnesium in 50 cc. of ether were heated 1 hour and then *slowly siphoned into* 10 grams of ethyl benzoylformate in 100 cc. of *cold* ether. With each drop was formed a precipitate of the bromomagnesium salt of the ethyl benzilate. When all of the Grignard reagent had been added, the white precipitate was filtered, washed once with absolute ether and shaken thoroughly with water. The ethyl benzilate and magnesium hydroxide precipitated and the latter was dissolved by the addition of dilute sulphuric acid. The ester was dissolved in ether, dried with calcium chloride and obtained as an oil weighing 9.0+ grams when the ether was evaporated. This liquid gave, with concentrated sulphuric acid, the beautiful color characteristic of ethyl benzilate and benzilic acid, but also the violet color characteristic of ethyl benzoylformate when benzene containing thiophene was added. When the mixture was fractionated *in vacuo* to separate the esters, we obtained 6 grams of ethyl benzilate, boiling at 194°–195° under 10 mm., and 3 grams of a mixture boiling at 130°–193° under 10 mm. The pure ethyl benzilate gave a deep red color with concentrated sulphuric acid. When boiled a short time with alcoholic potash the ester was converted into potassium benzilate; when this salt was dissolved in water and treated with dilute sulphuric acid, a white precipitate of benzilic acid was obtained. This melted at 150°–151° alone or when mixed with another sample of the pure acid. The ester was analyzed.

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[1] Ber. d. chem. Ges., **37**, 2753.

Analysis:

0.2007 gram substance gave 0.5524 gram CO_2 and 0.1144 gram H_2O.

	Calculated for $C_{16}H_{16}O_3$	Found
C	74.94	75.06
H	6.31	6.33

A similar experiment was tried with ethyl benzoylformate and *p*-tolylmagnesium bromide to obtain ethyl phenyl-*p*-tolylglycollate, $C_6H_5(C_7H_7)C(OH)COOC_2H_5$. Nearly all of the ethyl benzoylformate was recovered unchanged, but two grams of an ester boiling at 210°–212° under 15 mm. was also isolated. This has not yet been studied carefully.

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A STUDY OF THE HYDROGEN ELECTRODE, OF THE CALOMEL ELECTRODE AND OF CONTACT POTENTIAL

[FOURTH[1] COMMUNICATION ON STUDIES OF ELECTROMOTIVE FORCE]

BY C. N. MYERS AND S. F. ACREE

(We are indebted to the Carnegie Institution of Washington for aid in this work.)

I. INTRODUCTION

In a previous article,[2] the object of this investigation was stated as being the need of a direct, *very rapid* and accurate method for determining the hydrogen (also hydroxyl) ion concentration of dilute solutions. Such a method would be of special value in the study of many *organic* reactions involving, for example, the hydrolysis of salts or the saponification of esters, the reactions of addition products in cases of catalysis by hydrogen ions, and many others in which the system is gradually changing. The methods commonly in use heretofore have presented serious difficulties in their general application.

The work of H. G. Denham,[3] who measured the degree of hydrolysis of several inorganic salts and of aniline hydrochloride, has been particularly suggestive for the reason that he obtained results agreeing extremely well with those determined by Bredig by the conductivity method. The hydrogen electrode has been recognized by several[4] as a possible instrument for the solution of this problem, and with this in view the continuation of the present investigation has led to an attempt to make the hydrogen electrode an accurate instrument for measuring hydrogen ion concentrations; in other words, to make it a standard electrode.

In continuing this investigation, it was realized early that much of the accuracy of the work would be dependent upon the constancy and ease of reproduction of the calomel electrodes which were used with the hydrogen electrode. Furthermore, it seemed wise to make a more careful study of the hydrogen electrode than had been done by any one previous to this time. Upon investigation, it was found that considerable care in keeping the electrodes over long periods was quite essential in making the manipulation satisfactory, as well as accurate. More will be said concerning this particular point under the proper topic. To make the hydrogen electrode an accurate instrument for measuring hydrogen ion concentrations and to make the calomel cell more nearly standard, the measurements had to be made with a much higher degree of accuracy than has ordinarily been done up to the present time. In order to attain this result, the method of approaching the problem under consideration resolved itself into five lines of investigation:

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[1] THIS JOURNAL, **46**, 585, 621, 638.

[2] *Ibid.*, **46**, 585 (1911).

[3] J. Chem. Soc., **93**, 41 (1908).

[4] Desha: Diss., Johns Hopkins Univ., **1909.** THIS JOURNAL, **46**, 638. Loomis and Acree: *Ibid.*, **46**, 585–621. Lapworth, in private communications, and articles in the J. Chem. Soc.

I. A thorough and careful study of the calomel electrode. About sixty separate electrodes, arranged in batteries of ten, were prepared and intercompared with each other, so that the value adopted for the potential of the calomel electrode was the average of a number and not dependent upon a single electrode. Great care regarding purity of chemicals and cleanliness of apparatus was especially emphasized. Constancy and reproducibility under varying conditions were finally studied, the time period in some cases being as great as thirty (30) months.

II. Care of hydrogen electrodes and methods of keeping them constant so that they may be ready for use at any moment. Particular care was also taken in standardizing the acid used.

III. Measurements of the different systems. In order to obtain the most satisfactory measurements, it was found that there was need of considerable skill in manipulation, as well as of having both systems in the best possible condition previous to the comparison.

IV. Improvements in the apparatus. Temperature regulation has been found to be a very important factor in the measurement of the systems, so extreme precautions were taken along this line in the way of contacts on the relays, use of the master relay, cooling coil, heating coil of nichrome wire wound so that the amount of current could be easily regulated by means of switches. New[1] batteries for calomel electrodes, constant pressure apparatus and devices for keeping conditions constant were installed with most gratifying results.

V. Measurements of the following systems:

(*a*) H_2–Pt–0.1 N HCl
(*b*) 0.1 N KCl–HgCl–Hg
(*c*) 0.1 N HCl–HgCl–Hg
(*d*) Hg–HgCl–0.1 N HCl–0.1 N KCl–HgCl–Hg
(*e*) H_2–Pt–0.1 N HCl–0.1 N HCl–HgCl–Hg
(*f*) H_2–Pt–0.1 N HCl–0.1 N KCl–HgCl–Hg
(*g*) Hg–HgCl–0.1 N HCl $\overset{\text{Sandfüllung}}{\overline{\qquad\qquad}}$ 0.1 N KCl–HgCl–Hg
(*h*) Hg–HgCl–0.1 N HCl $\overset{\text{sat. KCl}}{\overline{\qquad\qquad}}$ 0.1 N KCl–HgCl–Hg

A few of the difficulties encountered in the use, the preservation and the reproducibility of the hydrogen electrode will be briefly described in this preliminary paper. First of all, we have not found in the literature any suggestion as to how to preserve the hydrogen electrode over long periods of time under conditions that would insure a degree of activity and constancy in keeping with the efforts of this investigation. It has been found very essential to keep the electrode in an *active* condition all of the time if the electrode is to be reproduced to within 0.00001 volt. This limit of reproducibility can be obtained quite easily with the proper care, and even better agreement is attainable, as some of our tables will show. During the previous summer the *dry* electrodes were carefully placed in a closed box with raw cotton. In the fall they were placed in 0.1 N hydrochloric acid and saturated with hydrogen, but the agreement between the individual electrodes was very poor, as will be noted in the first three lines of Table IV. After becoming dry and remaining so for some time, it is impossible to saturate the electrodes completely with hydrogen, as the platinum black is not in a condition to take up the hydrogen or even hold it. It became apparent at once that the most satisfactory method of *overcoming* this trouble was to *obviate* the difficulty in the first place. The electrodes were again electroplated with platinum black as described in the previous article, and considerable plating was required before they gave satisfactory agreement. However, all the electrodes (17 in number) were replatinized and, after some trouble, were made to agree to within about 0.00001 volt.

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[1] These do not have the ground-glass caps used by Loomis (THIS JOURNAL, 46, 595, 597, etc.), but are constricted and sealed at the top.

Among the other difficulties encountered were the effects of small amounts of impurities which were being dissolved from the commercial rubber stoppers[1] by the hydrochloric acid in which the electrodes were placed. A rubber stopper with 18 holes held the electrodes in place; in order to test their constancy, the electrodes must necessarily be in the acid for long intervals. We wanted them in measuring condition all the time. In order to avoid these impurities, a special mould was ordered in which *pure gum* stoppers were made for us and no further trouble was experienced. These are only a few incidents which show the sensitiveness of the hydrogen electrodes for detecting small amounts of foreign substances.

If satisfactory methods for measuring or calculating contact potential between various solutions were at hand, the hydrogen electrode could not be surpassed as an instrument for obtaining the ionization values of acids. If the hydrogen electrode is to be a standard electrode, it must be subjected to mechanical disturbance, transportation and use. In all of these particulars, experiment has shown the hydrogen electrode to be very satisfactory. The glass tube of one electrode became cracked at the place where the platinum wire is sealed into the electrode tube, and it was carefully wrapped and the glass sealed together with *no measurable bad effect* whatever on the electrode. Then again, the electrodes are moved around, taken out of the cylinders while acid is being replaced, and yet the same values for the individual electrodes are obtained as soon as saturation with hydrogen is reached. In comparing various systems involving the use of the hydrogen electrodes, these may be in use for four hours at a time and no change greater than the experimental error is ever detected.

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[1] For a description of the apparatus, see Loomis and Acree: THIS JOURNAL, **46**, 602.

Another device for obtaining better agreement between the individual electrodes, and *doing so in a very short time*, consists in the use of a short-circuiting arrangement in which all of the hydrogen (or calomel) electrodes are connected with each other through the mercury in the electrode tubes. We have termed this device a "crowfoot," and it is in use at all times when experiments are not being carried on. It will be seen at a glance that a much better agreement between the individual electrodes is obtained in a short time by its use. Occasionally, the electrodes will not show a variation greater than 0.000003 volt. This same device is used in connection with the calomel electrode with equally good results. When all of the different electrodes of a new calomel battery are connected by the "crowfoot," they attain values agreeing to within 0.00001 volt in about 2 days. If the "crowfoot" were not used, it would take about 5 days for them to agree as closely. As many as 40 hydrogen electrodes have been in use at one time. It seems better to use a great many electrodes, so that a measurement is not dependent upon one electrode but is the result of a comparison of a large number of them. No measurement is ever made unless all of the electrodes show a satisfactory agreement among themselves. The constancy of the electrodes has been tested over a period of nearly two years. It has been found that the amount of platinum black deposited on the electrodes is a factor which influences the relation between the individual electrodes. It is well known that changes in barometric pressure influence the concentration of hydrogen in the electrode and the solutions, so there is a lagging effect sometimes. It is quite analogous to the lagging effect noted in osmotic pressure. The point is that an electrode with a great deal of black on it does not respond as quickly to changes in the barometer and, hence, to changes in the amount of hydrogen present, thus causing changes in the individual readings of the potential of the electrodes. In due time, however, the values become more uniform; *i. e.*, saturation or changes in the degree of saturation are responded to finally. Of course, these changes of potential are not large, but when it is considered that 0.001 of an atmosphere causes a change of 0.000025 volt, it is easily seen that a few millionths of a volt can be the result of a sudden change in the barometer. Table IV gives a few points in the history of the electrodes.

Several investigators, and especially Bjerrum, have observed that in measuring any system in which the hydrogen electrode is a part there is a change in the value obtained at the beginning and an hour later, perhaps. This statement has led Dr. Myers to study this point to some extent, but we believe that we can offer a satisfactory explanation. If the systems 0.1 N KCl–HgCl–Hg and 0.1 N HCl–Pt–H_2 are to be compared, it is possible to connect them by satisfactory means and still obtain a changing value for the system if it is not first saturated with hydrogen. But suppose that the connecting system is first saturated with hydrogen, or, in other words, equilibrium is established and the systems are connected. Observations over periods of even a couple of hours show no changes whatever, provided no barometric change has taken place. Considerable emphasis has been given to this phase by Dr. Myers and we believe that in comparing these systems we are reasonably sure of our results to within 0.05 millivolt. Finally, it is our opinion that with saturated systems no changes in the value for any given system take place, other conditions remaining constant.

It is a well-known fact that the standard Clark or Weston element shows a gradual shift in its value, depending a great deal upon the age of the element. A similar shift has been observed by us in connection with the calomel electrode. In order to study this case, batteries have been made up from time to time and intercompared. At the present time, and with our present data, it appears that after standing a year the changes are very slow. We believe, as many others do, that this change or shift downward is due to the decomposition of the calomel:

$$2HgCl \rightleftharpoons HgCl_2 + Hg$$

At present, we have a pair of cells containing mercuric chloride in the presence of ordinary calomel and will compare these with old batteries. It would be expected that the relation of the potentials of the two systems would be practically zero if equilibrium is brought about quickly by mercuric chloride.

Only a few of the tables showing the relation of the various systems to each other are given in this paper. It should be stated here that we find the "Sandfüllung" method of Bjerrum very satisfactory and have used it to much advantage. A description of apparatus and technique will follow in later articles, in which measurements at constant temperature and constant pressure will be given. Constant pressure apparatus and a Fuess barometer accurate to within 0.05 mm. are used in connection with these systems.

Our reference cells are several Weston cells loaned us by the National Bureau of Standards and compared with their standards from time to time by Mr. E. C. McKelvey and Mr. Schumacher. We are greatly indebted to these gentlemen for much valuable advice and kindly interest. At present we are using 5 cells, Nos. 115, 117, 158, 197 and 201, and at other times we have used also Nos. 228, 231 and 251. That these standards check each other very closely is shown by the measurements given us on Oct. 4, 1912, for 28°:

Cell	115	117	158	197	201
E. m. f.	1.017847	1.017860	1.017838	1.017847	1.017851

These values are based on the international volt, which is taken as 1.0000/1.0183 of the electromotive force of the Weston normal cell at 20°. The temperature of our bath is 25° and the electromotive force at 25° is, therefore, 0.000155 volt greater than the above values. The average value of the five cells at 25° is, therefore, about 1.018000 volts. We check the cells against each other at frequent intervals on our potentiometer to assure ourselves that they are all in excellent agreement.

Our potentiometer was made for use with standard cells with the definition of the volt used prior to Jan. 1, 1911, and the lowest figure on the standard cell dial is 1.01850. Our cells set on this figure have really the value 1.01802, so all readings on the potentiometer must be corrected for the calibration of the potentiometer and then multiplied by 1.01802/1.01850. In addition we must add 0.000015 volt to those readings involving the hydrogen electrode, because of an error which we found in our old barometer when it was compared with a fine Fuess Normal Barometer. In the tables we give first the readings observed on the potentiometer and then the final reading, which we describe as "cor. ave." or "cor. value."

Experimental

In Table I we give the incomplete record of a 0.1 N KCl–HgCl–Hg battery, showing the changes taking place from the time the battery was first prepared. The numbers at the top of each column designate the number of each cell which composes the battery. All of the batteries are composed of ten cells each and this gives us an average value for this system for the reason that we always compare the entire set before making a measurement. These values are chosen haphazard and are a fair sample of the record of this battery. Six of these batteries have been prepared and intercompared so that the table also represents a fair record of the other batteries. It will be seen that about 36 to 48 hours are necessary for the cells to settle down, and over a period of twelve months the relation of the cells to No. I, chosen as a standard, has remained approximately constant. It is not to be understood that the entire system has not changed, for it has done so (see Table II*c*), in conformity with the observations of many others, probably as the result of a disintegration of the calomel in the following manner:

$$2\mathrm{HgCl} \rightleftarrows \mathrm{Hg} + \mathrm{HgCl_2}$$

The total change amounts to 0.000085 volt in a period of eight to ten months. Using the data of Abegg, in which the Hg'' ion concentration is given as 235 times as great as the Hg' ion concentration, we get a value 0.000090 volt, which is in close agreement with the experimental value found. Experiments in which mercuric chloride in extremely small amount is present are being carried out. The change observed between the individual cells of the calomel battery is smaller than in the case of the standard Weston element. The following values have been assigned to one of the elements by the U. S. Bureau of Standards: 1.01892, 1.01887, 1.01883 and 1.01783. Our total change in a battery has amounted to 0.000085 volt in one year, but the individual cells never vary this much.

Table I—Battery No. IV, 0.1 N KCl–HgCl–Hg[1]

Prepared May 2, 1912

18 hours after preparation the following values were recorded

Date	2	3	4	5	6	7	8	9	10
With Wires									
May 3, 1912	0.000140	0.000041	0.00001	0.000038	0.000026	0.00005	0.000025	0.000055	0.00018
May 4, 1912	0.000011	0.000005	0.000012	0.000008	0.000008	0.00008	0.000035	0.000002	0.000004
May 6, 1912	0.000015	0.000004	0.000006	0.000011	0.000004	0.000007	0.000002	0.000009	0.000005
May 7, 1912	0.000012	0.000007	0.000010	0.000013	0.000002	0.00003	0.000012	0.000015	0.000011
May 9, 1912	0.000001	0.000009	0.000009	0.000011	0.000010	0.000016	0.000010	0.00001	0.00003
Without Wires									
May 11, 1912	0.00005	0.00006	0.000015	0.00007	0.00006	0.00009	0.000045	0.00008	0.000075
With Wires									
May 22, 1912	0.000008	0.000009	0.000003	0.000007	0.000007	0.000010	0.000001	0.000009	0.000010
Apr. 11, 1913	0.000008	0.000007	0.000006	0.000007	0.000007	0.000007	0.000008	0.000008	0.000005

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[1] In this article we have omitted the signs showing whether these cells are + or — when compared with the reference cell. All such data will be presented in the final reports.

Table II*a* shows an intercomparison of two freshly prepared calomel batteries by using Cell No. 1 of each battery as the standard electrode. Table II*b* compares the same two batteries after a period of one year. The agreement in this latter case is even better than at the first comparison. The short-circuiting system is always used. In Table II*c* the relation between a freshly prepared calomel battery and one of a year's standing is given. The new battery is negative with respect to the old one, as would be expected. In the first three months, the difference of potential between the same batteries was about 0.000045 volt.

Table II—Comparison of Batteries B_{IV} and B_V

0.1 N KCl–HgCl–Hg

	a		*b*	*c*
	B_V compared against Cell I of B_{IV}		B_V compared with B_{IV} after 1 year. Cell I of B_V used as standard electrode	B_V compared with a fresh calomel battery
Cell	May 9	May 14		
1	0.000004	0.000007	0.000000	+0.000084
2	0.000001	0.000004	0.000003	0.000087
3	0.000007	0.000010	0.000000	0.000096
4	0.000009	0.000006	0.000002	0.000088
5	0.000010	0.000002	0.000002	0.000085
6	0.000009	0.000006	0.000002	0.000087
7	0.000010	0.000007	0.000006	0.000082
8	0.000004	0.000001	0.000004	0.000080
9	0.000009	0.000006	0.000006	0.000087
10	0.000003	0.000001	0.000001	0.000087

Table III gives a record of another battery, in which its history is very marked. Some oil got into the battery shortly after it was first made, but we decided to study the history of such a poor system and now give the data. The effect of the use and the non-use of the short-circuiting system is very clearly shown in this table. Where the words "without wires" appear, it indicates that the short-circuiting system was removed on the date appearing above these words. We realize that it is not one of our best batteries, but it shows that with a little trouble the reproducibility of the system is surely as good as 0.00001 volt. As stated above, a little oil crept in accidentally and for that reason the battery was not considered satisfactory and was prepared anew.

Table III—Battery No. II, 0.1 N KCl–HgCl–Hg

Prepared March 8, 1912. Electrode 1 as Standard

Readings taken two hours after the battery was placed in the bath

Date	2	3	4	5	6	7	8	9	10
Mar. 8	0.000460	0.000525	0.000300	0.000152	0.000370	0.000307	0.000570	0.000475	0.000120
Mar. 11	0.000134	0.000140	0.000103	0.000022	0.000082	0.000120	0.000185	0.000100	0.000035
Mar. 12	0.000065	0.000095	0.000045	0.000000	0.000046	0.000087	0.000125	0.000057	0.000024
Mar. 13	0.000095	0.000112	0.000070	0.000024	0.000018	0.000030	0.000072	0.000020	0.000000
Mar. 14	0.000085	0.000104	0.000060	0.00000	0.000062	0.000082	0.000100	0.000047	0.000055
Without Wires									
Mar. 15	0.000127	0.000160	0.000100	0.000045	0.000105	0.000122	0.000157	0.000065	0.000000
With Wires									
Mar. 16	0.000085	0.000110	0.000075	0.000075	0.000045	0.000100	0.000120	0.000070	0.000015
Mar. 19	0.000050	0.000073	0.000021	0.000000	0.000016	0.000030	0.000052	0.000013	0.000010
Without Wires									
Mar. 20	0.000082	0.000113	0.000020	0.000010	0.000024	0.000045	0.000082	0.000013	0.000020
With Wires									
Mar. 22	0.000030	0.000060	0.000002	0.000017	0.000001	0.000010	0.000035	0.000007	0.000030
Mar. 27	0.000035	0.000035	0.000000	0.000008	0.000004	0.000000	0.000005	0.000000	0.000026
Apr. 1	0.000022	0.000022	0.000007	0.000000	0.000002	0.000004	0.000005	0.000002	0.000004
Apr. 3	0.000020	0.000023	0.000006	0.000000	0.000000	0.000012	0.000008	0.000009	0.000002
Without Wires									
Apr. 5	0.000055	0.000062	0.000037	0.000050	0.000012	0.000035	0.000025	0.000037	0.000030
With Wires									
Apr. 9	0.000026	0.000026	0.000007	0.000001	0.000005	0.000016	0.000005	0.000012	0.000020
Apr. 12	0.000022	0.000020	0.000020	0.000022	0.000009	0.000024	0.0000120	0.000015	0.000007
Apr. 18	0.000015	0.000018	0.000004	0.000005	0.000007	0.000006	0.000004	0.000008	0.000022
Apr. 24	0.000006	0.000006	0.000005	0.000001	0.000005	0.000004	0.000003	0.000004	0.00002
Oil crept in before sealing and battery taken down									

Table IV—H_2–Pt–0.1 N HCl. Stopper I

Electrodes were placed in 0.1 N HCl after being left in box three months. H_2 allowed to run about five hours before first record was taken. Electrode 10 chosen as standard

Date, 1912	9	8	7	6	5	4	3	2	1
Jan. 18	*0.000186*	*0.00082*	*0.00047*	*0.00070*	*0.06293*	*0.000586*	*0.058810*	*0.000155*	*0.02558*
Jan. 19	0.000232	0.000178	0.000168	0.000169	0.004988	0.001736	0.003445	0.000696	0.00082
Jan. 20	0.000175	0.000081	0.000101	0.000195	0.002654	0.000895	0.001720	0.000405	0.000435
Electrodes replatinized and treated as described									
Jan. 22	0.00005	0.0000075	0.000227	0.00003	0.000636	0.000218	0.00043	0.000097	0.000073
Began use of "Crowfoot." Replatinized and electrolyzed									
Jan. 24	0.000015	0.000035	0.0000525	0.00004	0.000098	0.000031	0.000015	0.000015	0.000047
Jan. 26	0.000006	0.000010	0.000010	0.000010	0.000046	0.000009	0.000005	0.000025	0.000013
Jan. 27	0.000007	0.000003	0.000000	0.000005	0.000010	0.000006	0.000000	0.00004	0.000002
Jan. 31	0.000010	0.000006	0.000006	0.000003	0.000028	0.000006	0.000006	0.000037	0.000004
Rubber dissolving in acid as shown below									
Feb. 1	0.000042	0.000025	0.000046	0.000014	0.000046	0.000058	0.000044	0.000078	0.000044
Apparatus cleaned. Electrodes and stopper boiled in distilled water									
Feb. 4	0.000011	0.000015	0.000012	0.000006	0.000010	0.000018	0.000012	0.000025	0.000025
Feb. 6	0.000004	0.000004	0.000001	0.0000025	0.000003	0.000008	0.000002	0.000002	0.000005
Stove in bath burned out and temperature drops 6 degrees									
Feb. 9	0.000006	0.000003	0.000003	0.000005	0.000004	0.000002	0.000006	0.000006	0.000001
Without Wires									
Feb. 17	0.000025	0.00001	0.000015	0.000015	0.000014	0.000012	0.000009	0.000015	—[1]
Feb. 19	0.000020	0.000003	0.000015	0.000015	0.000026	0.000026	0.000025	0.000034	0.000027
Rubber dissolving in acid									
Mar. 6	0.00005	0.00006	0.00013	0.000055	0.000115	0.00009	0.00005	0.00014	0.000056
Electrodes boiled in distilled water and electrodes placed in constant pressure desiccator									
June 1	0.000020	0.000003	0.000005	0.000002	0.000003	0.000001	0.000001	0.000003	0.000000
Apr. 25, 1913	0.000005	0.000003	0.000006	0.000006	0.000007	0.000005	0.000004	0.000001	0.000003

[1] This electrode was broken and taken to Washington for repairs. When brought back to Baltimore on the same day and saturated again with hydrogen the values given below were obtained.

In Table IV, a record of the hydrogen electrode is given. In all, there are about 40 in use and only one section is given here. The record in this table shows the disagreement of the electrodes after standing dry all summer and the difficulty of getting them into close agreement. Many more readings have been recorded but these illustrate the essential changes. It should be noted that there is little change in the relation of the electrodes to each other on June 1 and on April 25, a period of nine months or more. The hydrogen electrode is reproducible to within 0.00001 volt, although the table shows even better agreement. This table also shows that the electrode is available at almost any moment when it is desired for use. The remaining electrodes are equally as good.

In Table V*a* a typical comparison of the hydrogen and *fresh calomel electrodes* and the methods of applying the correction are shown. The values *a, b, c, d are each averages of ten values* and have been corrected for the old barometer. Of the total 760 mm. pressure to which each of these readings corresponds, about 23.5 mm. is the partial pressure of the vapor above the acid and the remainder, about 736.5 mm., is the partial pressure of the hydrogen. In Table V*b* an average of 120 readings is given. These values are obtained by using different decinormal batteries on different dates, which means that the H′ ion concentration of the different hydrogen electrodes was perhaps slightly different at each time. The first six averages show increasing values, which would be expected for the reason that the calomel battery changes gradually and hence the potential of the system should increase. If, however, these values are all corrected for aging, it is found that the corrected average in Column 3 is 0.426910 volt, which is in very close agreement with all the values in Table V*a*, and with the last four values in Table *Vb*, which were obtained on Dec. 13, 1912, with *two fresh calomel batteries*.

Table Va—$Hg\text{-}HgCl\text{-}0.1\ N\ KCl\text{-}0.1\ N\ HCl\text{-}Pt\text{-}H_2$

Bar. in atms., 1.010; cor. in e. m. f., —0.000230

	0.427341
	0.427342
	0.427336
	0.427342
	0.427335
	0.427342
	0.427340
	0.427335
	0.427338
	0.427340
Ave.,	0.427339
Bar. cor.,	0.00023
	0.427109
Cor. ave.,	0.426919

	Other similar averages
	0.427106 (*a*)
	0.427109 (*b*)
	0.427109 (*c*)
	0.427108 (*d*)
Ave.,	0.427108
Cor. ave.,	0.426918

Table Vb

Apr. 1, 1912	0.427090	0.427090
Apr. 19, 1912	0.427108	0.427098
May 9, 1912	0.427112	0.427092
May 9, 1912	0.427115	0.427095
May 23, 1912	0.427123	0.427098
May 23, 1912	0.427126	0.427109
Dec. 13, 1912[1]	0.427106	0.427106
	0.427109	0.427109
	0.427109	0.427109
	0.427108	0.427108
Ave.,	0.427116	0.427100
Cor. ave.,	0.426926	0.426910

Table VI*a* gives a typical experiment and VI*b* an average of all such average readings taken when Bjerrum's "Sandfüllung" was used between the calomel and hydrogen electrodes. The final average represents about 100 separate electrode readings. The system compared is given at the top. The use of the "Sandfüllung" was to prevent the diffusion of the liquid from one system to the other.

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[1] These last four values were obtained from fresh calomel batteries.

Table VI—Hg–HgCl–0.1 N HCl$\frac{\text{Sandfüllung}}{}$*0.1 N HCl–Pt–*$H_2$

	a Bar. in atms., 1.004 Cor in e. m. f., —0.00010		b Corrected averages
	0.400100		
	(0.400470)		
	0.400080		0.400031
	0.400070		0.400081
	0.400080		0.400036
	0.400090		0.400020
	0.400090		0.400020
	0.400090		0.400020
	0.400070		
	0.400045	Ave.,	0.400035
		Cor. ave.,	0.399858
Ave.,	0.400080		
Bar. cor.,	0.000100		
	0.399980		
Cor. ave.,	0.399803		

Tables VII*a*, VII*b* and VII*c* give average values for the systems in question. When saturated potassium chloride was used in the connecting siphon, experiments with and without the "Sandfüllung" were carried out and no difference in the value of the potential was found.

Table VII*c* gives a typical contact potential experiment by the use of one Hg–HgCl–0.1 N HCl battery against a *fresh* calomel battery. It is plainly seen that the individual values are not as uniform as in the other systems but they are as good as the 0.1 N HCl–HgCl–Hg system is by itself. An average of several such averages is given in the other part of the table, showing the value placed for contact potential. No changing values are observed in this comparison. Readings were taken over a period of a couple of hours and they remained constant.

Table VIIa—H_2*–Pt–0.1 N HCl*$\frac{\text{Sandfüllung}}{\text{Sat. KCl}}$*0.1 N KCl–HgCl–Hg*

	Ave. value for system
	0.40120
	0.40114
	0.40120
Ave.,	0.401180
Cor. ave.,	0.401003

Table VIIb—H_2–Pt–0.1 N $\mathrm{HCl}\overset{\text{Sat. KCl}}{\text{———}}$0.1 N KCl–HgCl–Hg

	Ave. value for system
	0.401200
	0.401140
	0.401200
	0.401264
Ave.,	0.401200
Cor. ave.,	0.401023

Table VIIc—Hg–HgCl–0.1 N KCl–0.1 N HCl–HgCl–Hg

Contact Potential

	Several sets of values averaged		Readings from one Hg–HgCl–0.1 N HCl battery
	0.027863		0.028100
	0.027760		0.027910
	0.027775		0.027690
	0.027795		0.028190
			0.027610
Ave.,	0.027798		0.027610
Cor. ave.,	0.027785		0.027660
			0.027562
			0.027610
			0.027806
		Ave.,	0.027775
		Cor. ave.,	0.027762

This entire work will be summed up in a later article which will appear as a monograph. All apparatus and methods of experimentation will then be described in detail. One conclusion to be drawn at this time is the constancy in values of the various systems mentioned, which is explained by obtaining complete saturation with hydrogen before joining them.

Johns Hopkins University
June 1, 1913

[Contributions from the Chemical Laboratory of Harvard College]

ON THE PERKIN REACTION: A REPLY TO THE CRITICISM OF H. MEYER AND BEER[1]

By Arthur Michael

W. H. Perkin[2] found by heating benzoic aldehyde with acetic anhydride and sodium acetate, butyrate or valerate to 180° that in all cases cinnamic acid alone is formed and he concluded from these results that the reaction proceeds between the aldehyde and anhydride and not between the aldehyde and the salt. Fittig and Slocum[1] then took up the study of the mechanism of the Perkin synthesis and showed that heating a mixture of benzoic aldehyde, acetic anhydride and sodium acetate to 100° caused no reaction; when sodium butyrate in the place of the acetate was used, phenylangelic acid alone was slowly formed, but, when the experiment was done at 150°, a mixture containing 1 part of the above to 2 parts of cinnamic acid was obtained, and at 180° the proportion was 1 part of the first to 10 parts of the latter acid. Fittig[2] concluded from these results that at 100° the reaction proceeds between aldehyde and salt and explained the formation of cinnamic acid at higher temperature by assuming that the anhydride, under these conditions, first reacts on the salt to form sodium acetate. Therefore, according to this interpretation of the Perkin synthesis, which was generally accepted, it always proceeds between aldehyde and salt. Michael and Hartman[3] were led by theoretical considerations to doubt the validity of Fittig's proofs. They showed experimentally that it is only necessary to heat acetic anhydride for a short time at 100° with the sodium salts of butyric and caproic acids to obtain butyric and caproic anhydrides in excellent yields, while butyric anhydride does not act noticeably on sodium acetate under these conditions. These results prove unmistakably that in the Fittig and Slocum experiment of heating the aldehyde, acetic anhydride and sodium butyrate at 100°, the contents of the tube, after a short heating, must have consisted of aldehyde, considerable butyric anhydride and sodium acetate and but little, if any, acetic anhydride and sodium butyrate. As the reactions in the Perkin synthesis proceed very slowly, the formation of only phenylangelic acid under these conditions is a conclusive proof that the reaction proceeds between aldehyde and butyric anhydride with sodium acetate acting as a catalyzer, and, further, that Fittig's explanation of the formation of cinnamic acid at higher temperatures cannot be correct since sodium acetate was present in large proportion in the experiment at 100°, when no cinnamic acid was formed. Recently a further contribution to this interesting problem was made by H. Meyer and Beer,[1] who confirm Nef[2] in the fact that cinnamic acid is not formed by heating benzoic aldehyde, acetic acid and sodium acetate to 200°, but find that *o*-chlorocinnamic acid is obtained when a mixture containing *o*-chlorobenzoic aldehyde, instead of benzoic aldehyde, is subjected to these conditions. These chemists conclude, from this result, that the Perkin reaction does not proceed between the aldehyde and anhydride. A stable chemical system may become unstable by so changing one of its components as to increase its free *chemical* energy, by decreasing the chemical resistance which has to be overcome, or, if the reaction is dependent on the presence of a catalyzer, by using one of greater efficiency.[3] The first phase in the Perkin synthesis involves an aldolization:[4]

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[1] Monats. Chem., **34**, 649 (1913).

[2] J. Chem. Soc., **31**, 388 (1877).

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[1] Ann. Chem.`(Liebig), **277**, 53 (1885).

[2] *Ibid.*, **277**, 48.

[3] Ber. d. chem. Ges., **34**, 918 (1901).

$$R.CHO + CH_3\text{—} \longrightarrow R.CH(OH).CH_2\text{—}.$$

If the first step in the reaction cannot proceed in a given system it may be brought about by using an aldehyde whose carbonyl group has more free *chemical* energy, or by so changing the chemical character of the radical joined to the methyl group that the expense of energy necessary to separate one of its hydrogen atoms from the methyl carbon is diminished. Benzoic aldehyde does not react with acetic anhydride and sodium acetate at 200°, but by introducing a negative atom, or group, in the ortho position to the formyl group of the aldehyde we increase considerably the free *chemical* energy of its carbonyl group, which is now able to overcome the resistance due to the separation of hydrogen from the methyl carbon. Although a mixture of benzoic aldehyde, sodium acetate and glacial acetic acid may be heated to 200° without formation of cinnamic acid, Meyer and Beer[5] noticed its formation when potassium, instead of sodium, acetate is used. This result is in accordance with the fact that potassium salts show a far greater capacity to effect aldolization than the corresponding sodium derivatives.[1] These chemists have shown, too, that chlorocinnamic acid may be made, without employing acetic anhydride or acid, by heating *o*-chlorobenzoic aldehyde and potassium acetate, but to effect this result it is necessary to subject the mixture to a considerably higher temperature (240°). There is, of course, no reason why this autocatalytic synthesis should not be realized if, with the aid of a high temperature, the reactive carbonyl of chlorobenzoic aldehyde is able to overcome the hindrance to aldolization.

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[1] Monats. Chem., **34**, 649 (1913).

[2] Ann. Chem. (Liebig), **298**, 202 (1897).

[3] Michael: J. Am. Chem. Soc., **32**, 990 (1910).

[4] Fittig: Ann. Chem. (Liebig), **227**, 48 (1885).

Monats. Chem., **34**, 655.

The experiments of Meyer and Beer bring new evidence that the Perkin synthesis proceeds more difficultly with acetic acid than with acetic anhydride, and that it goes with still greater difficulty with potassium acetate. Instead, therefore, of disproving the view that, in the reaction of an aldehyde, acid anhydride and sodium salt of an aliphatic acid, which was solely the subject in the discussion of the Perkin reaction by Hartman and myself,[2] the first phase of the change consists of an aldolization between aldehyde and anhydride, they simply add a new set of facts to confirm this interpretation, which, indeed, is the only one in accordance with our present experimental knowledge of the subject.

[Contribution from the Chemical Laboratory of the University of Cincinnati]

APPLICATIONS OF THE ELECTRONIC CONCEPTION OF VALENCE

PART I. REACTIONS AMONG CERTAIN CLASSES OF COMPOUNDS CONTAINING NITROGEN

PART II. THE BECKMANN REARRANGEMENT

By Lauder William Jones

INTRODUCTION

Very convincing arguments have been presented in support of the hypothesis which regards electricity to be of such a nature that it "reacts" with atomic weights of the chemical elements in unit quantities, and, therefore, in accordance with the laws of definite and of multiple proportions. Notwithstanding the completeness with which this view has been presented in the abstract, comparatively few chemists[1] have ventured upon applications of it to concrete problems in organic chemistry, by which alone its usefulness in this field may be put to the test. In terms of the conception of valence which this hypothesis proposes, the processes of oxidation and reduction may be regarded as an exchange of electrons between atoms, a loss of negative electrons corresponding to oxidation and a gain in negative electrons to reduction. Thus, if two atoms, A and B, are linked together, the compound may be represented by two electronic formulas:

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[1] Michael and Kopp: This Journal, **5**, 182 (1883).

[2] The writer, therefore, does not consider the criticism of Meyer and Beer as relevant to the subject, nor is the fact (*Ibid.*, **34**, 656) that with one salt—rubidium acetate—the yield of chlorocinnamic acid was somewhat *larger* with acetic acid than with acetic anhydride. Only when the conditions of the experiments are absolutely comparable and when they can be repeated with the same result, should they be used as the basis for theoretical deductions.

$$\underset{\text{(I)}}{\mathrm{A}^{-}\,{}^{+}\mathrm{B}} \quad\longrightarrow\quad \underset{\text{(II)}}{\mathrm{A}^{+}\,{}^{-}\mathrm{B}}$$

If (I) passes to (II) by an exchange of negative electrons, A is said to be oxidized, while B is reduced.

Looked at from this angle, carbon with four as the valence of its atomic weight would show five stages in the series of oxidation and reduction, which may be illustrated by the following electronic symbols:[2]

$$\underset{\text{(I)}}{\mathrm{C}\overset{-}{\underset{-}{\substack{-\\-}}}} \qquad \underset{\text{(II)}}{\mathrm{C}\overset{+}{\underset{-}{\substack{-\\-}}}} \qquad \underset{\text{(III)}}{\mathrm{C}\overset{+}{\underset{-}{\substack{+\\-}}}} \qquad \underset{\text{(IV)}}{\mathrm{C}\overset{+}{\underset{-}{\substack{+\\+}}}} \qquad \underset{\text{(V)}}{\mathrm{C}\overset{+}{\underset{+}{\substack{+\\+}}}}$$

These symbols would represent the states of oxidation of the carbon atom in five compounds; viz., methane (I), methyl alcohol (II), formaldehyde (III),[1] formic acid (IV) and carbonic acid (V). Nitrogen presents a somewhat more complicated case. If it be considered as trivalent, and its two remaining or auxiliary valences disregarded, there are four types possible:

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[1] Schuetzenberger: Ann. Chem. (Liebig), **120,** 113 (1861). Seliwanow: Ber. d. chem. Ges., **25,** 3612 (1892). Noyes and Lyon: J. Am. Chem. Soc., **23,** 463 (1901). Stieglitz, *Ibid.*, **23,** 797 (1901); **29,** 51 (1903); Science, **30** (1907); Qualitative Chem. Analysis, I and II, p. 29 (1911); *Ibid.*, III, p. 82 (1911). Walden: Z. physik. Chem., **43,** 407 (1903); **46,** 103 (1903). Abegg: Z. anorg. Chem., **39,** 343 (1903). Thomson, J. J.: Phil. Mag., March, 1904; "The Corpuscular Theory of Matter," p. 130 (1907). Nef: J. Am. Chem. Soc., **30,** 645 (1908). Ramsay: J. Chem. Soc., **93,** 774 (1908). Falk and Nelson: School of Mines Quarterly, **30,** 179 (1909); J. Am. Chem. Soc., **32,** 1673 (1910); **33,** 1140 (1911); Congress of Applied Science, **6,** 282 (1912). Fry: Z. physik. Chem., **76,** 385, 398, 591 (1911); **77,** 29 (1912); J. Am. Chem. Soc., **34,** 664 (1912). Jones: This Journal, **48,** 25 (1912). Noyes: J. Am. Chem. Soc., **34,** 662 (1912); **35,** 767 (1913). Acree: This Journal, **49,** 347 (1913).

[2] Fry: Z. physik. Chem., **76,** 399 (1911). Stieglitz: Science, **30** (1907).

$$\begin{array}{cccc}
\mathrm{N}\begin{matrix}-\\-\\-\end{matrix} & \mathrm{N}\begin{matrix}+\\-\\-\end{matrix} & \mathrm{N}\begin{matrix}+\\+\\-\end{matrix} & \mathrm{N}\begin{matrix}+\\+\\+\end{matrix} \\
\mathrm{(I)} & \mathrm{(II)} & \mathrm{(III)} & \mathrm{(IV)}
\end{array}$$

These symbols correspond to the states of oxidation of the nitrogen atom in ammonia (I), hydroxylamine (II), dihydroxylamine (hyponitrous acid) (III), and nitrous acid (IV). If quinquivalent nitrogen is represented in a similar way, there are six electronic symbols, exclusive of stereoisomeric configurations:

$$\begin{array}{cccccc}
\mathrm{N}\begin{matrix}-\\-\\-\\-\\-\end{matrix} & \mathrm{N}\begin{matrix}+\\-\\-\\-\\-\end{matrix} & \mathrm{N}\begin{matrix}+\\+\\-\\-\\-\end{matrix} & \mathrm{N}\begin{matrix}+\\+\\+\\-\\-\end{matrix} & \mathrm{N}\begin{matrix}+\\+\\+\\+\\-\end{matrix} & \mathrm{N}\begin{matrix}+\\+\\+\\+\\+\end{matrix} \\
\mathrm{(I)} & \mathrm{(II)} & \mathrm{(III)} & \mathrm{(IV)} & \mathrm{(V)} & \mathrm{(VI)}
\end{array}$$

All but (I) yield compounds in corresponding states of oxidation with respect to the nitrogen atom. Thus, ammonium compounds correspond to (II); hydroxylammonium compounds and amine oxides, $R_3N : O$, to (III); isonitroparaffins to (IV); nitro compounds to (V); and derivatives of nitric acid to (VI). It will be noted that in all cases where nitrogen functions as trivalent, the two remaining or auxiliary valences must be one negative and one positive. Taking this into consideration the four symbols used to represent trivalent nitrogen become identical with symbols (II), (III), (IV) and (V), among those representing quinquivalent nitrogen.[2] Com-

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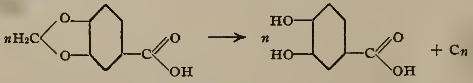
[1] It is noteworthy that, taken as a whole, the carbon atom in formaldehyde is neither negative nor positive. This suggests an explanation of the observation that some of the derivatives of formaldehyde decompose and deposit elemental carbon. Thus, piperonylic acid when heated with hydrochloric acid to 150° gave carbon:



[2] Univalent nitrogen would be represented by the two symbols N^+ and N^-. The auxiliary valences must be two positive and two negative. That is, we should expect to obtain univalent nitrogen derivatives from compounds which contain nitrogen either in the state of oxidation corresponding to hydroxylamine, or to dihydroxylamine (hyponitrous acid), and from these alone.

pounds represented by formulas containing nitrogen linked to nitrogen, N-N, may be indicated by proper combinations of the various symbols given.

Amines, Aldimides, Nitriles and Nitrile Oxides.—An inspection of the chemical transformations characteristic of four classes of organic compounds, viz., primary amines of the type $R.CH_2.NH_2$, aldimides, $R.CH : NH$, nitriles, $R.C \vdots N$, and nitrile oxides, $R.C \vdots N{:}O$—and of a number of other organic compounds which may be grouped about them in a very intimate way—suggested certain applications of the electronic hypothesis which seem to throw new light upon the chemical relations between these compounds, and to indicate a mechanism in terms of which their transformations may be portrayed more precisely than by the ordinary structural formulas now in vogue.

If, for the sake of clearness only, the monomolecular forms are considered, these four compounds plainly represent a series of products which may be grouped as successive stages in the oxidation of the primary amine, $R.CH_2.NH_2$. Thus:

$$\underset{\text{Amine}}{R.CH_2.NH_2} \longrightarrow \underset{\text{Aldimide}}{R.CH{:}NH} \longrightarrow \underset{\text{Nitrile}}{R.C \vdots N} \longrightarrow \underset{\text{Nitrile oxide}}{R.C \vdots N{:}O}$$

Each of the three oxidation products of the primary amine may be considered as a transition compound, and may be placed schematically between two isomers formally derivable from it by the addition of one molecule of water. The amine may also be included in this table, together with the products of hydrolysis which it may be imagined to yield by the breaking of the carbon-nitrogen linking with the addition of water in the two possible directions.

	A	B	C
1	$R.CH_3 + NH_2OH$	$R.CH_2.NH_2$	$R.CH_2.OH + NH_3$
2	$R.CH_2.NHOH$	$R.CH : NH$	$R.CH(OH).NH_2$
3	$R.CH : NOH$	$R.C \vdots N$	$R.C(OH) : NH$
4	$R.CH : \underset{\underset{O}{\Vert}}{N}OH$	$R.C \vdots N : O$	$R.C(OH) : NOH$

Thus, the amine lies between a hydrocarbon and hydroxylamine on the one hand and an alcohol and ammonia on the other;

the aldimide falls between a β-substituted hydroxylamine and an aldehyde ammonia; the nitrile is related to an aldoxime and an amide, while the nitrile oxide is associated with an isonitro compound and a hydroximic acid.

It will be noted that the compounds represented in Column A of this table have never been made by the hydrolysis of the corresponding transition compounds in Column B; these transition compounds upon hydrolysis always yield substances whose formulas stand opposite them in Column C.

In this connection some of the actual experiments carried out by Bamberger and others are worthy of mention. In a series of articles, Bamberger[1] and his co-workers have presented the results obtained in the oxidation of primary, secondary and tertiary amines with Caro's acid. Ethylamine[2] upon oxidation gave acetaldoxime, acetonitrile, acetic acid, ammonia, nitroethane and acethydroxamic acid. The first step in the oxidation, β-ethylhydroxylamine, could not be detected. With tertiary butylamine, however, Bamberger and Seligman obtained β-tertiarybutylhydroxylamine, $(CH_3)_3C.NHOH$. Benzylamine[3] gave benzaldoxime, benzonitrile, benzaldehyde, ammonia, benzamide, benzoic acid, benzhydroxamic acid and phenylnitromethane. In a similar fashion, starting with one of the higher oxidation products, acetaldoxime, Bamberger obtained chiefly nitroethane and acethydroxamic acid. Benzaldoxime[4] (20.7 grams) gave benzaldehyde (0.3 gram), benzoic acid (7.6 grams), benzamide (trace), phenylnitromethane (2.3 grams), benzhydroxamic acid (2.6 grams) and nitric acid. Bamberger assumed that the first step in the process of oxidation should be represented by the direct addition of oxygen to the nitrogen; this mechanism was proposed because of the ease with which tertiary amines were oxidized to amine oxides, $R_3N : O$.

These experiments show conclusively that during the oxidation of an amine, $R.CH_2.NH_2$, with Caro's acid, the nitrile is the only one of the three transition compounds actually isolated, but that the three pairs of related isomers, viz., β-substituted hydroxylamines and aldehyde ammonias, aldoxime and amide, isonitroparaffin and hydroxamic acid, or products formed from them by hydrolysis (aldehydes, acids, ammonia, hydroxylamine) appear in almost every case.

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[1] Bamberger and Tschirner: Ber. d. chem. Ges., **31**, 1522 (1898); **32**, 342, 1675 (1899).

[2] Bamberger: *Ibid.*, **35**, 4293 (1902).

[3] Bamberger and Scheutz: *Ibid.*, **34**, 2029, 2262 (1901).

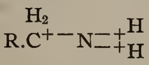
[4] Bamberger: *Ibid.*, **33**, 1781 (1900).

Hydrolysis as a Means of Determining the State of Oxidation of the Nitrogen and the Carbon Atoms.—Since the four transition compounds and the three pairs of corresponding isomers may all be hydrolyzed, it would seem to be permissible to draw conclusions concerning the state of oxidation of the carbon atom and of the nitrogen atom in each one from the products of hydrolysis; at least, such products would indicate the state of oxidation which must have prevailed within the molecule *immediately preceding the separation of the carbon atom from the nitrogen atom.* In the following discussion, it is proposed to use this principle as a guide to interpret the mechanism of hydrolysis in the case of these various classes of organic compounds, the object being to see whether the electronic conception of valence is of any real assistance as a working hypothesis in these particular cases, and then to apply it in other cases of a similar character to be found at every turn in organic chemistry.

PART I. REACTIONS AMONG CERTAIN CLASSES OF COMPOUNDS CONTAINING NITROGEN

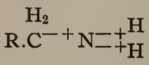
1. The Relations between Amines, $R.CH_2.NH_2$, and their Products of Hydrolysis

Amines may be hydrolyzed, but with some difficulty. In every case, however, the nitrogen is eliminated as ammonia, and an alcohol (phenol) forms the second product. In terms of the electronic conception of valence, we are led by these facts to represent the linking between the carbon atom and the nitrogen atom in the amine by electronic formula (I):



$R.\overset{H_2}{C}{}^{+}{-}N\begin{matrix}{-}{+}H\\{-}{+}H\end{matrix}$

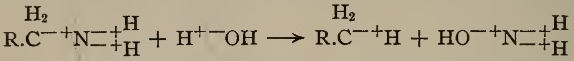
Amine (I)



$R.\overset{H_2}{C}{}^{-}{+}N\begin{matrix}{-}{+}H\\{-}{+}H\end{matrix}$

Amine (II)

The electromere corresponding to Formula II does not seem to have a real existence, since such a formula for the amine would demand that the products of hydrolysis be a hydrocarbon on the one hand and hydroxylamine on the other. Thus:

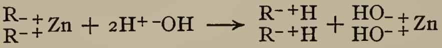


$$R.\overset{H_2}{C}{}^{-+}N\begin{matrix}-+H\\-+H\end{matrix} + H^{+-}OH \longrightarrow R.\overset{H_2}{C}{}^{-+}H + HO^{-+}N\begin{matrix}-+H\\-+H\end{matrix}$$

But, as yet, these products have never been found among the substances actually obtained by hydrolyzing the amine.

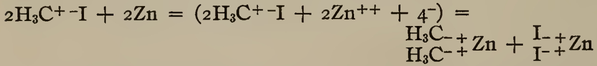
These considerations would seem to lead to the conclusion *that a carbon atom when linked directly to a nitrogen atom does not readily take from it negative electrons, or, in other words, is not readily reduced by it.* This conclusion will be strengthened by evidence presented in connection with other classes of compounds discussed later in this article.

The conditions appear to be quite the reverse with certain elements like zinc, magnesium, etc., which form metal-organic compounds. Thus, zinc dialkyls, when hydrolyzed, give hydrocarbons and zinc hydroxide. In view of this fact, the formulas of zinc alkyls and their hydrolysis must be represented by the following electronic symbols:



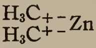
$$\begin{matrix}R_{-}{}^{+}\\R^{-+}\end{matrix}Zn + 2H^{+-}OH \longrightarrow \begin{matrix}R^{-+}H\\R^{-+}H\end{matrix} + \begin{matrix}HO_{-}{}^{+}\\HO^{-+}\end{matrix}Zn$$

The synthesis of zinc dimethyl from methyl iodide and zinc, omitting for convenience the intermediate stage R.Zn.I, may be illustrated by the equations which follow:



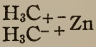
$$2H_3C^{+-}I + 2Zn = (2H_3C^{+-}I + 2Zn^{++} + 4^{-}) = \begin{matrix}H_3C_{-}{}^{+}\\H_3C^{-+}\end{matrix}Zn + \begin{matrix}I_{-}{}^{+}\\I^{-+}\end{matrix}Zn$$

The electronic formula used for methyl iodide is justified by the fact that methyl iodide yields methyl alcohol and hydrogen iodide upon hydrolysis.[1] If zinc dimethyl were represented by the electronic formula



$$\begin{matrix}H_3C_{+}{}^{-}\\H_3C^{+-}\end{matrix}Zn$$

it should be resolved by hydrolysis into methyl alcohol and zinc hydride; and if the electronic formula were



$$\begin{matrix}H_3C_{+}{}^{-}\\H_3C^{-+}\end{matrix}Zn$$

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[1] Abegg: Z. anorg. Chem., **39**, 373 (1903).

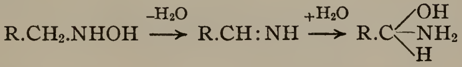
it should yield methane, methyl alcohol and zinc, or by direct dissociation ethane and zinc. Consequently, in the linking $C^{+}{}^{-}Zn$, we must assume a process of oxidation and reduction in which the zinc atom is oxidized and the carbon atom is reduced, or, in terms of the hypothesis, the zinc atom loses two negative electrons which are gained by the carbon atom.

2. *The Relations between Aldimides, β-Alkyl(aryl)hydroxylamines and Aldehyde Ammonias*

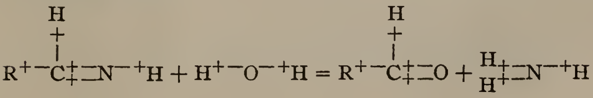
When aldimides, R.CH : NH, are hydrolyzed they yield aldehyde ammonias, or ultimately aldehydes and ammonia. This change requires the addition of water to the aldimide and must be represented by formulas in which hydrogen passes to nitrogen and the hydroxyl group to carbon:

$$R.CH:NH + HOH = R.CH(OH).NH_2$$

It may be imagined, however, that the molecule of water might be added in the reverse direction, viz., hydrogen to carbon and hydroxyl to nitrogen, which would lead to the formation of a β-substituted hydroxylamine. An inspection of the usual formula, R.CH : NH, brings to light nothing which would prevent such a theoretical conclusion, and it is only the initiated who can unerringly predict that hydrolysis will lead to the formation of an aldehyde and ammonia by reading into the formula more than it actually contains. In other words, the reactions expressed in the following equations might be reversible:



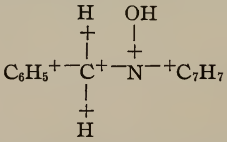
But there is not a single experimental result which substantiates this supposition; aldimides always yield ammonia and an aldehyde, and never by hydrolysis alone β-substituted hydroxylamines. These facts would demand the following electronic formula for aldimides. The equation also represents the process of their hydrolysis:



$$R^{+}{}^{-}\overset{\overset{\displaystyle H}{+}}{\underset{+}{\overset{+}{C}}}{}^{=}_{=}N^{-}{}^{+}H + H^{+}{}^{-}O^{-}{}^{+}H = R^{+}{}^{-}\overset{\overset{\displaystyle H}{+}}{\underset{+}{\overset{+}{C}}}{}^{=}_{=}O + {}^{H^{+}}_{H^{+}}{}^{=}_{=}N^{-}{}^{+}H$$

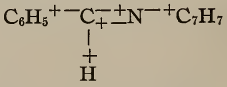
Although β-substituted hydroxylamines and β-disubstituted hydroxyalmines are not known to be formed by the hydrolysis of aldimides or of substituted aldimides, R.CH : NR, it has been shown that both classes of compounds in the presence of mild dehydrating agents are converted, probably through aldimides, into aldehydes and ammonia (or amines). It seems plausible, therefore, to assume that this change is brought about by a loss of water between carbon and nitrogen in one direction and an addition of water in the reverse direction in the manner indicated by the equation given above. Thus, Walder[1] found that β-dibenzylhydroxylamine, $(C_7H_7)_2NOH$, with an excess of acetyl chloride gave chiefly benzaldehyde and benzylamine. The same transformation was brought about by treating the compound with acetic acid in which hydrogen chloride was dissolved ("Beckmann's mixture"). Behrend and Leuchs[2] stated that benzaldehyde and benzylamine were formed by the direct splitting of β-dibenzylhydroxylamine into these two products. In a footnote to Walder's article, Victor Meyer[3] spoke of the reaction as an "intramoleculare Selbstoxydation."

This reaction presents a number of interesting features when it is considered from the electronic point of view. It is evident that β-dibenzylhydroxylamine must be regarded as a derivative of hydroxylamine and benzyl alcohol:



$$\begin{array}{cccc}
 & \mathrm{H} & \mathrm{OH} & \\
 & + & | & \\
 & | & + & \\
\mathrm{C_6H_5}^{+} & {}^{-}\mathrm{C}^{+} & {}^{-}\mathrm{N}^{-} & {}^{+}\mathrm{C_7H_7} \\
 & | & & \\
 & + & & \\
 & \mathrm{H} & &
\end{array}$$

By a loss of one molecule of water, an electromere of the following formula would be expected:



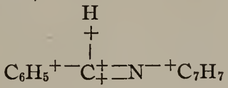
$$\begin{array}{cccc}
\mathrm{C_6H_5}^{+} & {}^{-}\mathrm{C}\,{}^{\mp}\,{}^{\pm} & \mathrm{N}^{-} & {}^{+}\mathrm{C_7H_7} \\
 & | & & \\
 & + & & \\
 & \mathrm{H} & &
\end{array}$$

[1] Walder: Ber. d. chem. Ges., **19**, 1629, 3287 (1886).

[2] Behrend and Leuchs: Ann. Chem. (Liebig), **257**, 233 (1890).

[3] Walder: *Loc. cit.*, 1629 (note).

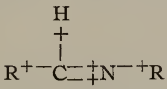
But by hydrolysis alone this electromere could not yield benzylamine and benzaldehyde. It would either regenerate the original β-dibenzylhydroxylamine, or be decomposed into β-monobenzylhydroxylamine and benzyl alcohol. Consequently, before benzylamine and benzaldehyde can be formed there must be an "intramoleculare Selbstoxydation" as Victor Meyer called it, or the carbon atom must yield negative electrons which are at once combined with the nitrogen atom to give a new electromere,



$$\mathrm{C_6H_5}^{+}{-}\overset{\substack{\mathrm{H}\\+\\|}}{\mathrm{C}}{}^{+}_{+}{=}\mathrm{N}{-}{}^{+}\mathrm{C_7H_7}$$

This electromere, and this one alone, can explain the formation of benzylamine and benzaldehyde.

Assuming that R and H linked to carbon are both positive,[1] one other electronic formula may be written



$$\mathrm{R}^{+}{-}\overset{\substack{\mathrm{H}\\+\\|}}{\mathrm{C}}{=}{}^{+}_{+}\mathrm{N}{-}{}^{+}\mathrm{R}$$

But this formula could not represent the aldimide obtained from β-disubstitued hydroxylamines since, upon hydrolysis, it would yield a hydrocarbon and a derivative of dihydroxylamine (a nitroso compound or an oxime).

3. The Relations between Nitriles, Aldoximes and Amides

Nitrile I.—Under the influence of reagents which of themselves possess neither oxidizing nor reducing properties, a *syn*-aldoxime loses one molecule of water, and a nitrile is produced. But when water is added to this same nitrile, the resulting compound is always an amide, or finally ammonia and a carboxylic acid, and never the original aldoxime from which the nitrile was obtained by loss of water. These changes are usually represented by structural formulas which show that water is lost by the aldoxime in one direction, and that the amide is formed by the addition of water in the reverse direction to the carbon-nitrogen linking of the nitrile:

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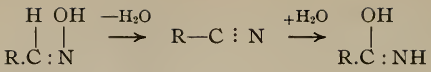
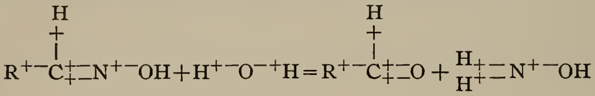
[1] If either R or H is negative, or if both R and H are negative, it is evident that other electronic formulas are conceivable.



$$R.\overset{\overset{H}{|}}{C}:\overset{\overset{OH}{|}}{N} \xrightarrow{-H_2O} R{-}C \vdots N \xrightarrow{+H_2O} R.\overset{\overset{OH}{|}}{C}:NH$$

An inspection of this reaction, however, leads to the conclusion that the nitrile, which one might expect from the aldoxime, should be an electromere of the nitrile which yields the amide, and that it could not be identical with it, a conclusion which is suggested in no way whatsoever by the usual structural formula, $R.C \vdots N$.

This statement will be evident if one recalls that the aldoxime, when hydrolyzed, gives an aldehyde and hydroxylamine. That is, the carbon-nitrogen linking must be represented by some combination of the symbols $\substack{+\\+}C\substack{-\\-}$ and $N\substack{+\\-\\-}$. Consequently, the electronic formula of the aldoxime and the course of its hydrolysis may be shown by the following equation:



$$R^{+-}\overset{\overset{H}{+}}{\overset{|}{C}}\substack{+\\+}\substack{-\\-}N^{+-}OH+H^{+-}O^{-+}H=R^{+-}\overset{\overset{H}{+}}{\overset{|}{C}}\substack{+\\+}\substack{-\\-}O+\substack{H\\H}\substack{+\\+}\substack{-\\-}N^{+-}OH$$

In view of these relations, it would seem logical to assume that a loss of water by the aldoxime should give, at least transiently, an electromere of the following formula:

$$R^{+-}C\substack{-\,+\\+\,-\\+\,-}N$$

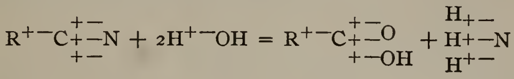
Nitrile (I)

and that a nitrile of this particular formula should regenerate the aldoxime, or, at any rate, when completely hydrolyzed, would given an aldehyde and hydroxylamine.

Nitrile II.—Now, a nitrile which would yield an amide, or ammonia and a carboxylic acid, could result from this electromere (I) by intramolecular oxidation; that is, by an exchange of negative electrons between carbon and nitrogen:

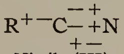
$$\underset{\text{Nitrile (I)}}{R^{+-}C\substack{-\,+\\+\,-\\+\,-}N} \longrightarrow \underset{\text{Nitrile (II)}}{R^{+-}C\substack{+\,-\\+\,-\\+\,-}N}$$

Since all known nitriles, when hydrolyzed, give amides (or ammonia and carboxylic acids), and never an aldoxime or an aldehyde and hydroxylamine, it is to be inferred that they should be represented by the electronic formula (II). The hydrolysis would then be indicated as follows:



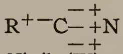
$$\mathrm{R}^{+-}\mathrm{C}\underset{+-}{\overset{+-}{+-}}\mathrm{N} + 2\mathrm{H}^{+-}\mathrm{OH} = \mathrm{R}^{+-}\mathrm{C}\begin{matrix}\overset{+-}{+-}\mathrm{O}\\ +-\mathrm{OH}\end{matrix} + \begin{matrix}\mathrm{H}_{+-}\\ \mathrm{H}+-\mathrm{N}\\ \mathrm{H}^{+-}\end{matrix}$$

When the radical R is regarded as positive,[1] it is self-evident that in addition to the two nitrile formulas already given, two other electronic formulas are possible, viz.:



$$\mathrm{R}^{+-}\mathrm{C}\underset{+-}{\overset{-+}{-+}}\mathrm{N}$$

Nitrile (III)



$$\mathrm{R}^{+-}\mathrm{C}\underset{-+}{\overset{-+}{-+}}\mathrm{N}$$

Nitrile (IV)

A nitrile of Formula (III) by hydrolysis would yield an alcohol and dihydroxylamine (or hyponitrous acid), while one of Formula (IV) would give a hydrocarbon and nitrous acid. Although no nitriles possessing these properties are known, it seems highly probable that they are formed as transition products in certain reactions.

Nitrile III.—Thus, Seliwanow[2] pointed out the hypochlorous character of chlorine in monochloro- and dichloroamines, $RNHCl$ and $RNCl_2$, and in nitrogen trichloride, NCl_3. This was made evident by the fact that all of the chlorine in these compounds could be eliminated as hypochlorous acid. Seliwanow determined the amount of iodine liberated by the action of compounds of the formula $RNHCl$ upon an acidulated solution of potassium iodide, and found that, for every atomic weight of chlorine in these compounds, two atomic weights of iodine were liberated. Previous to this time, Schuetzenberger[3] had prepared compounds of the type R.C(OCl) : O and had suggested that chlorine, in these compounds, played

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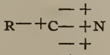
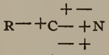
[1] If R is negative, there are four other electronic formulas which can be written



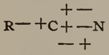
$$\mathrm{R}^{-+}\mathrm{C}\underset{-+}{\overset{-+}{-+}}\mathrm{N}$$

(V)



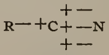
$$\mathrm{R}^{-+}\mathrm{C}\underset{-+}{\overset{+-}{-+}}\mathrm{N}$$

(VI)



$$\mathrm{R}^{-+}\mathrm{C}\underset{-+}{\overset{+-}{+-}}\mathrm{N}$$

(VII)



$$\mathrm{R}^{-+}\mathrm{C}\underset{+-}{\overset{+-}{+-}}\mathrm{N}$$

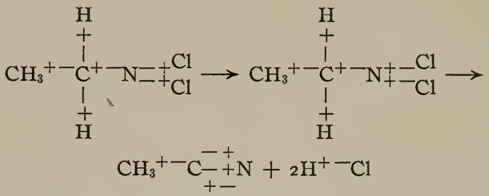
(VIII)

[2] Seliwanow: Ber. d. chem. Ges., **25**, 3617 (1892). Noyes: J. Am. Chem. Soc., **35**, 767 (1913).

[3] Schuetzenberger: Ann. Chem. (Liebig), **120**, 113 (1861).

the role of an electropositive metal in the salts. In terms of the electronic conception of valence, chlorine in all of these compounds must be considered as positive, Cl^{+}.[1]

By the action of alcoholic potash upon dichloroethylamine, $C_2H_5NCl_2$, Seliwanow obtained potassium acetate, ammonia and potassium chloride. In terms of the present mode of viewing the reaction, the following equation would indicate the course of the reaction:



$$CH_3{}^{+}{-}\underset{\underset{H}{+}}{\overset{\overset{H}{+}}{C}}{}^{+}{-}N\begin{smallmatrix}-+Cl\\ -+Cl\end{smallmatrix} \longrightarrow CH_3{}^{+}{-}\underset{\underset{H}{+}}{\overset{\overset{H}{+}}{C}}{}^{+}{-}N\begin{smallmatrix}+-Cl\\ +-Cl\end{smallmatrix} \longrightarrow$$

$$CH_3{}^{+}{-}C\begin{smallmatrix}-\,+\\ -\,+\\ +\,-\end{smallmatrix}N + 2H^{+}{-}Cl$$

It will be observed that the nitrile here represented would correspond to nitrile (III) shown above. This nitrile, however, by intramolecular oxidation, must pass at once to the usual electromere (I), $CH_3{}^{+}{-}C\begin{smallmatrix}-\,+\\ -\,+\\ +\,-\end{smallmatrix}N \longrightarrow CH_3{}^{+}{-}C\begin{smallmatrix}+\,-\\ +\,-\\ +\,-\end{smallmatrix}N$, which, in turn, would give the products actually obtained by Seliwanow, viz., acetic acid and ammonia. Similar changes have been observed by Berg[2] in the study of the chlorine derivatives of secondary amines, RR′NCl. Thus, ethylamylamine chloride, $(C_2H_5)(C_5H_{11})NCl$, with alkalis gave either acetaldehyde, amylamine and a chloride (KCl), or valeric aldehyde, ethylamine and a chloride. In a previous article,[3] I suggested that similar reactions accompany the Beckmann rearrangement of bromo amides according to the Hofmann method.

From these reactions, the conclusion may be drawn that, in alkaline solutions at least, a system $>C\begin{smallmatrix}-\,+\\ +\,-\end{smallmatrix}\underset{|}{\overset{+H}{N}}-{}^{+}Cl$ tends to pass to a system $>\mathrm{C}\substack{-\ +\\+\ -}\overset{\mathrm{H}}{\underset{|}{\mathrm{N}}}{}^{+}{}^{-}\mathrm{Cl}$, which, in turn, by an exchange of negative electrons between carbon atom and the nitrogen atom, with the loss of $\mathrm{H}^{+}{}^{-}\mathrm{Cl}$, finally becomes $>\underset{|}{\mathrm{C}}\substack{+\\+}\substack{-\\-}\mathrm{N}$.

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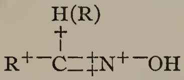
[1] Noyes: J. Am. Chem. Soc., **23**, 463 (1901). Stieglitz: *Ibid.*, **23**, 769 (1901); **29**, 51 (1903). Walden: Z. physik. Chem., **43**, 407–43 (1903). J. J. Thompson: The Corpuscular Theory of Matter, p. 130 (1907).

[2] Berg: Bull. soc. chim., [3] **17**, 297 (1897).

[3] Jones: This Journal, **48**, 26 (1912).

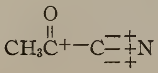
Nitrile IV.—It will be recalled that oximes are frequently prepared by the action of nitrous acid or amyl nitrite upon compounds containing methylene groups, $\mathrm{R.CH_2.R'}$, especially when R or R′ are so-called negative groups (e. g., RC : O). Furthermore, certain derivatives of nitrous acid (NOCl, $\mathrm{N_2O_3}$) may be added to olefin hydrocarbons, and to hydrocarbons of the hydroaromatic series. The latter reaction plays a very important role in the study of the terpenes. If the nitroso compounds obtained by the addition of these reagents contain a grouping $>\mathrm{C}\begin{smallmatrix}\diagup\mathrm{H}\\ \diagdown\mathrm{N:O}\end{smallmatrix}$ in their formulas, a rearrangement may be brought about to give oximes $>\mathrm{C : NOH}$.

For example, amyl nitrite, in the presence of sodium ethylate, converts acetone into isonitrosoacetone, $\mathrm{CH_3.CO.CH{:}NOH}$. If reactions of this kind consisted merely in the loss of alcohol or water, whether intermediate products in the nature of addition products are assumed or not, the oximes which would be formed must be assigned the electronic formula



$$\mathrm{R}^{+}{}^{-}\overset{\substack{\mathrm{H(R)}\\+\\|}}{\mathrm{C}}\substack{-\\-}\substack{+\\+}\mathrm{N}^{+}{}^{-}\mathrm{OH}$$

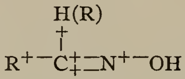
that is, the nitrogen must still be in the state of oxidation which it has in nitrous acid. When isonitrosoacetone, prepared in the manner described above, is treated with acetic anhydride, a nitrile, acetyl cyanide, is formed. Assuming that the electronic formula just given represents the state of oxidation in isonitrosoacetone, acetyl cyanide, which differs from it by one molecule of water, must receive the following electronic formula:



$$\mathrm{CH_3}\overset{\substack{\mathrm{O}\\\|}}{\mathrm{C}}{}^{+}{}^{-}\mathrm{C}\substack{-\\-\\-}\substack{+\\+\\+}\mathrm{N}$$

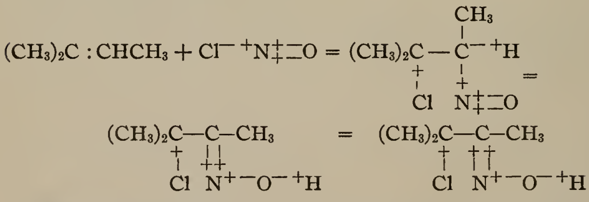
If our reasoning were correct, this nitrile should be a nitrile of Formula (IV) previously indicated.

But oximes prepared by the methods described are not different in chemical behavior from oximes prepared by the action of hydroxylamine upon carbonyl compounds;[1] they all yield hydroxylamine and a carbonyl compound upon hydrolysis, and never nitrous acid accompanied by the original methylene derivative. Furthermore, the nitriles (e. g., acetyl cyanide) obtained from these aldoximes always give ammonia and a carboxylic acid and not nitrous acid which would be demanded if the formula given above were correct. Consequently, all such reactions with nitrous acid must involve not merely a loss of water, but also a simultaneous intramolecular oxidation and reduction in which the carbon atom loses negative electrons, and the final state must be shown by the electronic formula



$$R^{+}{}^{-}\overset{\substack{H(R)\\+\\|}}{C}\overset{+}{\underset{+}{|}}\!\overset{-}{\underset{-}{=}}N^{+}{}^{-}OH$$

In a similar manner, the addition of nitrosyl chloride and of nitrous anhydride to unsaturated compounds leads to the formation of oximes by processes of rearrangement and simultaneous intramolecular oxidation. Thus:



$$(CH_3)_2C:CHCH_3 + Cl^{-}\,{}^{+}N\overset{+}{\underset{+}{|}}\!\overset{-}{\underset{-}{=}}O = (CH_3)_2\underset{\substack{+\\|\\Cl}}{C}-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\+\\N\overset{+}{\underset{+}{|}}\!\overset{-}{\underset{-}{=}}O}}{C}}{}^{-}\,{}^{+}H =$$

$$(CH_3)_2\underset{\substack{+\\|\\Cl}}{C}-\underset{\substack{|\,|\\+\,+\\N^{+}{}^{-}O^{-}{}^{+}H}}{C}-CH_3 = (CH_3)_2\underset{\substack{+\\|\\Cl}}{C}-\underset{\substack{+\,+\\|\,|\\N^{+}{}^{-}O^{-}{}^{+}H}}{C}-CH_3$$

From these considerations it may be inferred that the existence of nitriles of the formulas $R^{+}{}^{-}C\substack{-\,+\\-\,+\\-\,+}N$, or $R^{+}{}^{-}C\substack{-\,+\\-\,+\\+\,-}N$ is highly improbable, and that even if they should occur transiently in reactions similar to those described above, they would be transformed at once by intramolecular oxidation and reduction into the stable and usual form $\mathrm{R}^{+}\,{}^{-}\mathrm{C}\begin{smallmatrix}+\,-\\+\,-\\+\,-\end{smallmatrix}\mathrm{N}$.

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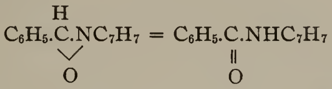
[1] Thus, violuric acid may be prepared by the action of nitrous acid upon malonylurea or by the action of hydroxylamine upon mesoxalylurea.

Isoaldoximes.—Beckmann[1] studied the behavior of isoaldoximes. In the presence of acid chlorides, or of hydrogen chloride dissolved in acetic acid ("Beckmann's mixture"), benzylisobenzaldoxime, which gave benzaldehyde and β-benzylhydroxylamine upon hydrolysis, was converted into benzylbenzamide:



$$\underset{\diagdown\!\diagup\;O}{\overset{H}{C_6H_5.C.NC_7H_7}} = \underset{O}{\underset{\|}{C_6H_5.C.NHC_7H_7}}$$

It is surprising how easily this change may be accomplished. According to Beckmann, 0.0456 gram of acetyl chloride was sufficient to cause the rearrangement of one gram of benzylisobenzaldoxime. It will be evident that this change must be accompanied by a transfer of electrons between carbon atom and the nitrogen atom, since the isoaldoxime, which yields benzaldehyde and β-benzylhydroxylamine, must be represented by some combination of the symbols $\begin{smallmatrix}-\\-\end{smallmatrix}\mathrm{C}\begin{smallmatrix}+\\+\end{smallmatrix}$ and $\mathrm{N}\begin{smallmatrix}+\\-\\-\end{smallmatrix}$, while benzylbenzamide, which yields benzylamine and benzoic acid upon hydrolysis, must be represented by the symbols $\begin{smallmatrix}+\\+\end{smallmatrix}\mathrm{C}\begin{smallmatrix}+\\-\end{smallmatrix}$ and $\mathrm{N}\begin{smallmatrix}-\\-\\-\end{smallmatrix}$.

4. *The Relations between Nitrile Oxides, Isonitroparaffins and Hydroximic Acids*

The Conversion of Nitro Compounds into Hydroxamic Acids.—Shortly after Victor Meyer[2] announced that nitroparaffins could be prepared by the action of halogen alkyls upon silver nitrite, Preibisch[3] observed that primary nitroparaffins heated with concentrated hydrochloric acid gave fatty acids and hydroxylamine. At that time, this reaction was considered very remarkable; for it was not apparent how the hydrolysis of a nitro compound, a derivative of nitrous acid, could give hydroxylamine.

[1] Beckmann: Ber. d. chem. Ges., **26**, 2272 (1893).

[2] V. Meyer: Ann. Chem. (Liebig), **171**, 19 (1872).

[3] Preibisch: J. prakt. Chem., [2] **7**, 480 (1873); **8**, 316 (1874). V. Meyer and Locher: Ann. Chem. (Liebig), **180**, 163 (1876).

Somewhat later, Nef[1] found that a solution of sodium isonitromethane, when mixed with mercuric chloride, gave some mercuric fulminate. Since the study of the fulminates had induced him to look upon fulminic acid as carbon monoxide oxime, HON : C, a derivative of bivalent carbon, here again was a case in which a nitro compound, by comparatively simple chemical reactions, had been converted into a derivative of hydroxylamine.

Jones[2] advanced the view that the formation of hydroxylamine and fatty acid, as well as the conversion of isonitromethane into fulminate, had a common cause, viz., the preliminary transformation of the isonitroparaffin into a hydroximic acid:

$$\mathrm{R.CH : NO(OH) \longrightarrow R.\c{C}(OH) : NOH}$$

Support was given to this interpretation by the singular behavior of the primary isonitroparaffin salts towards acid chlorides. Jones[3] found that sodium isonitroethane, CH_3CH :-N(ONa) : O, reacted with benzoyl chloride but that the benzoyl ester of the isonitroparaffin could not be obtained; in its stead, the benzoyl ester of acethydroxamic acid was formed.

$$\mathrm{CH_3.CH : N(OCOC_6H_5) : O \longrightarrow CH_3.C(OH) : N.OCOC_6H_5}$$

This reaction was described as a case of intramolecular oxidation, and the intimate relation existing between isonitro compounds and hydroxamic acids was dwelt upon in the interpretation.

Subsequently, this interrelation was brought out more emphatically by Bamberger[4] who observed that hydroxamic acids were formed in small amounts when solutions of the salts of certain primary isonitro compounds were poured into dilute mineral acids. Later, Bamberger[5] brought about the change directly by heating phenylnitromethane with sulphuric acid, and was able to prove that benzhydroxamic acid was one of the products of the reaction:

$$\mathrm{C_6H_5.CH : N(OH) : O \longrightarrow C_6H_5.C(OH) : NOH}$$

[1] Nef: Ann. Chem. (Liebig), **280**, 275 (1894).

[2] Jones: This Journal, **20**, 35 (1898).

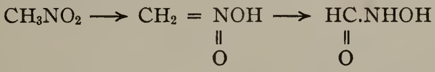
[3] Jones: *Loc. cit.*, p. 2. Van Raalte: Rec. trav. chim., **18**, 378 (1899).

[4] Bamberger and Rust: Ber. d. chem. Ges., **35**, 47 (1902).

[5] Bamberger: *Loc. cit.*, p. 52. Cazeneuve: Compt. rend., **198**, 244.

In the case of *p*-nitrophenylnitromethane, heated to 130° with sulphuric acid (65 parts concentrated acid to 100 parts of water), he isolated *p*-nitrobenzhydroxamic acid in considerable amount without any difficulty. Furthermore, it may be recalled that Bamberger found both nitro compounds and hydroxamic acids among the products which resulted when primary amines were oxidized with Caro's acid (p. 418).

The surprising ease with which, at times, this transformation may occur is strikingly illustrated by an observation recently reported by Angeli[1] who found that nitromethane itself, when exposed to light, first showed a change to isonitromethane, and that later small amounts of formhydroxamic acid could be shown to be present:



$$CH_3NO_2 \longrightarrow CH_2 = \underset{\underset{O}{\|}}{N}OH \longrightarrow H\underset{\underset{O}{\|}}{C}.NHOH$$

Nitrile Oxides.—By the action of sodium carbonate upon chlorobenzhydroximic acid, $C_6H_5.CCl : NOH$, Werner and Buss[2] prepared benzonitrile oxide. The monomolecular form, to which they assigned the formula $C_6H_5.C \vdots N : O$, was not isolated by them, but only a dimolecular polymer which they considered to be diphenylglyoxime peroxide. Later, by a more careful treatment of chlorobenzhydroximic acid with sodium carbonate, Wieland[3] obtained benzonitrile oxide in its monomolecular form as a solid melting at 15°. It showed a remarkable tendency to polymerize, and gave not only two dimolecular polymers, diphenylfuroxan and dibenzoxoazoxime, but also a trimolecular form.

Benzonitrile oxide, when reduced, gave benzonitrile, but, strange to say, an attempt to prepare the nitrile oxide by the oxidation of benzonitrile with Caro's acid failed. When either the monomolecular form or its polymers were heated with indifferent solvents (benzene, toluene) they were changed into phenyl isocyanate. Because of the failure of the nitrile oxide to react by addition with ammonia, aniline, bromine, etc., Wieland[1] preferred the formula $\underset{\mathrm{O}}{\underbrace{C_6H_5.C : N}}$ to the one proposed by Werner and Buss, but the evidence does not seem to be altogether convincing.

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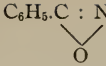
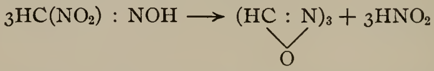
[1] Angeli: Ber. d. chem. Ges., **45**, 1775 (1912).

[2] Werner and Buss: Ber. d. chem. Ges., **27**, 2199 (1894).

[3] Wieland: *Ibid.*, **40**, 418 (1907); **42**, 803 (1909).

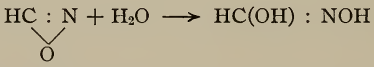


By the action of sodium carbonate upon methylnitrolic acid, Wieland succeeded in making the simplest nitrile oxide, formonitrile oxide, but only in a trimolecular form, a yellow explosive solid which he called trifulmine:



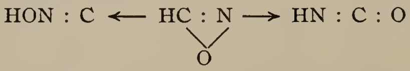
$$3HC(NO_2) : NOH \longrightarrow (\underset{\mathrm{O}}{\underbrace{HC : N}})_3 + 3HNO_2$$

The hydrolysis of trifulmine presents many interesting features. With acids, hydroxylamine salts and formic acid were produced. Concentrated hydrochloric acid gave considerable formyl chloride oxime (HON : CHCl), through which trifulmine could be converted into silver fulminate (Nef).[2] If water alone was used, the chief product was *formhydroxamic acid,*



$$\underset{\mathrm{O}}{\underbrace{HC : N}} + H_2O \longrightarrow HC(OH) : NOH$$

while alkalis gave isocyanate (or carbonate and ammonia). Wieland pointed out that formonitrile oxide might be expected to yield either fulminic acid or isocyanic acid since it is isomeric with these two substances:



$$HON : C \longleftarrow \underset{\mathrm{O}}{\underbrace{HC : N}} \longrightarrow HN : C : O$$

There is no mention, however, in Wieland's articles of the conversion of formonitrile oxide into isonitromethane by the addition of water, a change which would not seem to be altogether improbable in view of the fact that methylnitrolic acid, the source of trifulmine, is prepared by the action of nitrous acid upon isonitromethane:

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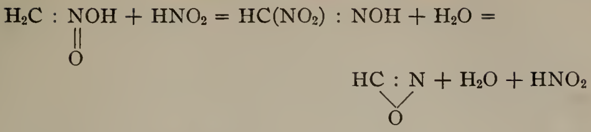
[1] Ber. d. chem. Ges., **40**, 1669 (1907).

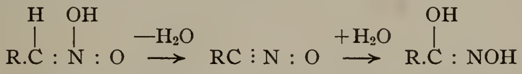
[2] Nef: Ann. Chem. (Liebig), **280**, 310 (1894).



$$H_2C : \underset{\overset{\|}{O}}{N}OH + HNO_2 = HC(NO_2) : NOH + H_2O = \underset{\overset{\diagdown\diagup}{O}}{HC : N} + H_2O + HNO_2$$

A superficial inspection of these equations would lead to the conclusion that the net result of the reactions is a loss of one molecule of water by the isonitromethane, since HNO_2 in the first equation and in the last equation would cancel.

The nitrile oxides, therefore, seem to form transition compounds which may be placed between the isonitro compound and the hydroximic acid in much the same way that nitriles lie between aldoximes and amides:



$$R.\overset{\overset{H}{|}}{C} : \overset{\overset{OH}{|}}{N} : O \xrightarrow{-H_2O} RC \vdots N : O \xrightarrow{+H_2O} R.\overset{\overset{OH}{|}}{C} : NOH$$

In the light of Wieland's recent experiments, it seems highly probable that careful experimentation would lead to the direct preparation of nitrile oxides from primary isonitro compounds by processes of dehydration similar to those employed in making nitriles from aldoximes. In fact, several year ago, Hantzsch[1] subjected phenylisonitromethane, $C_6H_5.CH : N(:O)OH$, to the action of phosphorus pentachloride and of phenyl isocyanate. Violent reactions occurred in both cases; treatment with phenyl isocyanate gave *diphenylurea* and oily products which he did not succeed in resolving into pure substances. In the literature, I have found only one instance of the direct conversion of a nitro compound into a nitrile oxide. When silver nitrite reacts with ethyl monobromoacetate, no ethyl nitroacetate was produced. In its place, a compound differing from it by one molecule of water was obtained to which Scholl and Schoefer[2] assigned the formula

$$C_2H_5O.C(:O).C \vdots N : O$$

It was accompanied by a dimolecular form. Both of these compounds when reduced gave glycocoll. Here would seem to be a case in which a nitro compound, by loss of water, had passed directly into a nitrile oxide. Recently, Steinkopf[1] has prepared nitroacetic acid and some of its derivatives. He found that the ammonium salt of nitroacetamide in the presence of thionyl chloride, even at 50°, was converted into β-oximinooxalimino chloride, a hydroximic acid derivative of oxalic acid:

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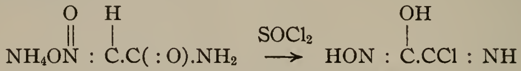
[1] Hantzsch: Ber. d. chem. Ges., **32**, 614, 620 (1899).

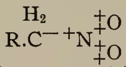
[2] Scholl and Schoefer: *Ibid.*, **34**, 870 (1901).



$$NH_4O\overset{\overset{O}{\|}}{N} : \overset{\overset{H}{|}}{C}.C(:O).NH_2 \xrightarrow{SOCl_2} HON : \overset{\overset{OH}{|}}{C}.CCl : NH$$

Electronic Formulas of Nitroparaffins and Isonitroparaffins.—There are two important methods of making nitro compounds, viz., by the action of nitric acid upon hydrocarbons, and by the action of a nitrite upon halogen alkyls (aryls).

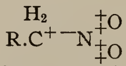
The preparation of nitro derivatives by the direct nitration of hydrocarbons with loss of water would point to the formation of compounds in which the nitrogen atom might be assumed to persist in the state of oxidation which it had in nitric acid.[2] If this were so, the primary nitro compound would have the following electronic formula:



$$R.\overset{H_2}{C}^{-}\;{}^{+}N\begin{smallmatrix}\overset{+}{\underset{+}{}}O\\ \overset{+}{\underset{+}{}}O\end{smallmatrix}$$

Nitro compound (I)

On the other hand, their formation from halogen compounds and nitrites would suggest a formula in which the nitrogen still has the state of oxidation corresponding to that in nitrous acid:



$$R.\overset{H_2}{C}^{+}\;{}^{-}N\begin{smallmatrix}\overset{+}{\underset{+}{}}O\\ \overset{+}{\underset{+}{}}O\end{smallmatrix}$$

Nitro compound (II)

Direct hydrolysis does not lead to a choice between these two electromeres, for primary nitro compounds obtained from either source give chiefly hydroxylamine and a carboxylic acid, and not nitric acid or nitrous acid accompanied by a hydrocarbon or an alcohol. Since, however, the primary nitro compounds

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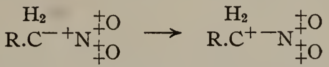
[1] Steinkopf: J. prakt. Chem., **81**, 97, 193.

[2] It is interesting to note that Hantzsch (Ber. d. chem. Ges., **32**, 637 (1899)) found that trinitroethane, with potassium hydroxide, gave dinitroethane and potassium nitrate:

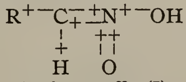
$$CH_3C(NO_2)_3 + KOH = CH_3CH(NO_2)_2 + KNO_3.$$

obtained by the two processes are identical, Formula (II) seems the more plausible; and from previous results described in this paper it may be concluded that an electromere of Formula (I) would tend to pass into one of Formula (II) by an exchange of negative electrons between the carbon atom and the nitrogen atom:



$$\overset{H_2}{R.C}{}^{-}\,{}^{+}N\begin{matrix}{}^{+}_{+}O\\{}^{+}_{+}O\end{matrix} \longrightarrow \overset{H_2}{R.C}{}^{+}\,{}^{-}N\begin{matrix}{}^{+}_{+}O\\{}^{+}_{+}O\end{matrix}$$

Isonitro Compounds.—Primary nitro compounds prepared by either method are changed into salts of isonitro compounds by the action of alkalis or sodium ethylate. Provided this change is a rearrangement pure and simple, the isonitro compound obtained from the nitro compound of formula (II) would have the following formula:



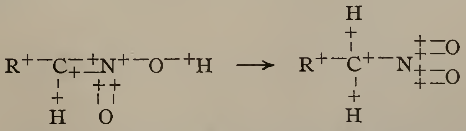
$$R^{+-}\underset{\substack{|\\+\\H}}{C}{\mp}{\pm}\underset{\substack{++\\||\\O}}{N}{}^{+-}OH$$

Isonitroparaffin (I)

This conclusion seems to be verified by experiments with salts of the isonitro compounds. It is a well-known fact that very careful treatment of solutions of isonitroparaffin salts with exactly one equivalent of acid leads to the separation of the *aci*-nitroparaffin,[1] which in turn reverts to the nitro compound itself:

RCH : N(: O)ONa+HCl ⟶ RCH : N(: O)OH+NaCl

In some cases both the *aci*-form and the nitro compound have been isolated as solids. The *aci*-form is always labile and passes more or less readily into the stable nitro compound. Formula (I) assigned to the isonitro compounds easily explains these changes:



$$R^{+-}\underset{\substack{|\\+\\H}}{C}{\mp}{\pm}\underset{\substack{++\\||\\O}}{N}{}^{+-}O^{-+}H \longrightarrow R^{+-}\overset{\substack{H\\+\\|}}{\underset{\substack{|\\+\\H}}{C}}{}^{+-}N\begin{matrix}{}^{+}_{+}{=}O\\{}^{+}_{+}{=}O\end{matrix}$$

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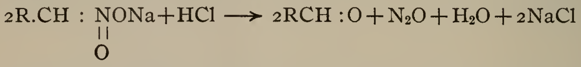
[1] V. Meyer: Ber. d. chem. Ges., **27**, 31, 56 (1894); **28**, 202 (1895). Nef: Ann. Chem. (Liebig), **280**, 266 (1894); Ber. d. chem. Ges., **29**, 1223 (1896). Hantzsch: *Ibid.*, **32**, 613 (1899).

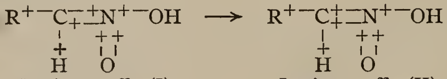
When, however, an excess of acid was used in acidifying the solution of the salt of the isonitro compound, very different results were obtained. Nef[1] showed that salts of primary isonitroparaffins, when treated with an excess of dilute mineral acid, gave chiefly nitrous oxide and an aldehyde:



$$2\mathrm{R.CH}:\underset{\substack{||\\ \mathrm{O}}}{\mathrm{N}}\mathrm{ONa}+\mathrm{HCl}\longrightarrow 2\mathrm{RCH}:\mathrm{O}+\mathrm{N_2O}+\mathrm{H_2O}+2\mathrm{NaCl}$$

In addition to these products, he found only traces of nitrous acid, with some fatty acid and hydroxylamine, the latter formed probably by the hydrolysis of the hydroxamic acid, which Bamberger[2] has shown to be one of the products of these reactions. The mercuric chloride salt of isonitroethane, $C_2H_4NO_2.HgCl$, with an excess of acid, gave as much as 98 per cent. of the amount of nitrous oxide calculated.[3] Sodium isonitroethane according to Nef[4] gave 89.4 per cent. of the calculated amount of nitrous oxide. The striking difference in behavior when an exact equivalent of acid was used is shown by experiments reported by Hantzsch,[5] who succeeded in regenerating nitroethane to the extent of nearly 100 per cent. when great care was taken to avoid excess of acid and to maintain a low temperature.

The conclusions to be drawn from these experiments must be that Formula (I) assigned to isonitroparaffins cannot represent the isonitroparaffin *as it participates in this reaction;* that is to say, it could not explain the formation of aldehyde and nitrous oxide, since the carbon-nitrogen linking in Formula (I) corresponds to alcohol and nitrous acid. Therefore, in the presence of an excess of acid, isonitroparaffin (I) must change to a second electromere:



$$\mathrm{R}^{+}{}^{-}\underset{\substack{|\\ +\\ \mathrm{H}}}{\mathrm{C}}{}^{-}_{+}{}^{+}_{-}\underset{\substack{++\\ ||\\ \mathrm{O}}}{\mathrm{N}}{}^{+}{}^{-}\mathrm{OH}\longrightarrow \mathrm{R}^{+}{}^{-}\underset{\substack{|\\ +\\ \mathrm{H}}}{\mathrm{C}}{}^{+}_{+}{}^{-}_{-}\underset{\substack{++\\ ||\\ \mathrm{O}}}{\mathrm{N}}{}^{+}{}^{-}\mathrm{OH}$$

Isonitroparaffin (I) Isonitroparaffin (II)

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[1] Nef: *Loc. cit.*, p. 266.

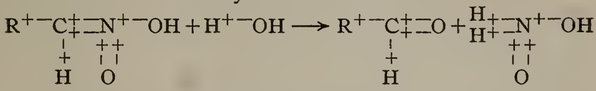
[2] Bamberger and Rust: Ber. d. chem. Ges., **35**, 47 (1902).

[3] Nef: Ann. Chem. (Liebig), **280**, 272 (1894).

[4] Nef: *Loc. cit.*, p. 268.

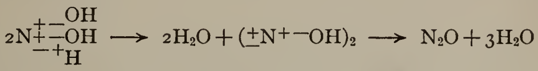
[5] Hantzsch and Veit: Ber. d. chem. Ges., **32**, 618 (1899).

An electromere having this formula (II) would explain the decomposition of the salts of primary isonitroparaffins by an excess of acid into aldehyde and nitrous oxide:



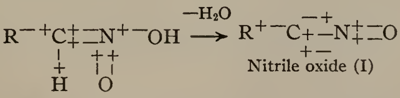
$$R^{+-}\underset{\substack{|\\+\\H}}{C}\ddagger\!=\!\underset{\substack{++\\||\\O}}{N}{}^{+-}OH + H^{+-}OH \longrightarrow R^{+-}\underset{\substack{|\\+\\H}}{C}\ddagger\!=\!O + \begin{smallmatrix}H\\H\end{smallmatrix}\!\!{}^{+}_{+}\!\!=\!\underset{\substack{++\\||\\O}}{N}{}^{+-}OH$$

By rearrangement, this form, $H_2N(OH) : O$, would give dihydroxylamine, then hyponitrous acid, and finally nitrous oxide and water:



$$2N\begin{smallmatrix}{}^{+}\!-OH\\ +\!-OH\\ -{}^{+}H\end{smallmatrix} \longrightarrow 2H_2O + (\pm N^{+-}OH)_2 \longrightarrow N_2O + 3H_2O$$

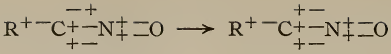
Isonitro Compounds and Hydroxamic Acids.—The fact that in all of these reactions small amounts of hydroxamic acids make their appearance, and that certain primary nitro compounds by the action of moderately concentrated sulphuric acid may be changed into hydroxamic acids, demands an explanation. The assumption has already been made (p. 433) that nitrile oxides form the intermediate products in this transformation in much the same way that aldimides and nitriles may be regarded as intermediate stages in the transformation of β-substituted hydroxylamines and aldoximes into aldehyde ammonias and amides. The conditions met with here are very similar to those discussed in the previous cases. That is to say, the nitrile oxide formed from an isonitro compound of Formula (II) cannot be the nitrile oxide which gives a hydroximic acid by the addition of water, but must be an electromere of it:



$$R^{-+}\underset{\substack{|\\+\\H}}{C}\ddagger\!=\!\underset{\substack{++\\||\\O}}{N}{}^{+-}OH \xrightarrow{-H_2O} R^{+-}C\overset{-+}{\underset{+-}{+\!-}}N\ddagger\!=\!O$$

Nitrile oxide (I)

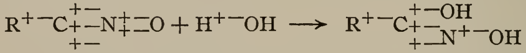
A nitrile oxide of this formula (I) would be hydrolyzed to give an aldehyde and nitrous oxide. Therefore, before a hydroxamic acid can be formed, there must be an exchange of electrons between the carbon atom and the nitrogen atom, and a second electromere must result:



$$\mathrm{R}^{+}\,{}^{-}\mathrm{C}\overset{-\,+}{\underset{+\,-}{\substack{+\\-}}}\mathrm{N}\substack{+\\+\\+}\substack{-\\-}\mathrm{O} \longrightarrow \mathrm{R}^{+}\,{}^{-}\mathrm{C}\overset{+\,-}{\underset{+\,-}{\substack{+\\-}}}\mathrm{N}\substack{+\\+\\+}\substack{-\\-}\mathrm{O}$$

Nitrile oxide (I) Nitrile oxide (II)

This conclusion is justified by the fact that all nitrile oxides, as well as all hydroxamic acids, when hydrolyzed, give hydroxylamine and a carboxylic acid. The readiness with which nitrile oxides yield hydroxamic acids is emphasized by the experiments of Wieland[1] with formonitrile oxide and aceonitrile oxide:



$$\mathrm{R}^{+}\,{}^{-}\mathrm{C}\overset{+\,-}{\underset{+\,-}{\substack{+\\-}}}\mathrm{N}\substack{+\\+\\+}\substack{-\\-}\mathrm{O} + \mathrm{H}^{+}\,{}^{-}\mathrm{OH} \longrightarrow \mathrm{R}^{+}\,{}^{-}\mathrm{C}\substack{+\,-\,\mathrm{OH}\\+\,-\\+\,-}\mathrm{N}^{+}\,{}^{-}\mathrm{OH}$$

Summing up all of these changes, we see that, in the case of the primary nitroparaffins, the state of oxidation of the carbon atom and of the nitrogen atom linked together tends to pass from the system $\substack{-\\-}\mathrm{C}\substack{-\\-}$ and $\mathrm{N}\substack{+\\+\\+\\+\\+}$ to a system $\substack{-\\+}\mathrm{C}\substack{+\\+}$ and $\mathrm{N}\substack{+\\+\\-\\-\\-}$; that is, to substances which are hydrolyzed to give a carboxylic acid and hydroxylamine. These observations would seem to justify the assumption previously made that a carbon atom when linked directly to a nitrogen atom does not readily take from it negative electrons or, in other words, is not readily reduced by it.

5. *The Relations between Hydroxamic Acids, Isocyanates and Carbamic Acids*

At least one more transition is possible, viz., a change which would give a system in which the carbon-nitrogen linking would contain carbon in a state of oxidation corresponding to that which it has in carbonic acid ($\substack{+\\+}\mathrm{C}\substack{+\\+}$) and nitrogen in a state of reduction corresponding to that which it has in ammonia $\left(\mathrm{N}\substack{+\\-\\-\\-\\-}\right)$.

Such a transformation is nicely illustrated by formhydroxamic acid which, in the presence of alkalis, gives isocyanates, carbamates, or carbonates and ammonia.[2]

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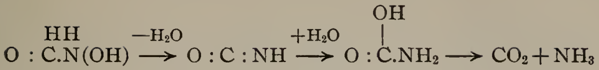
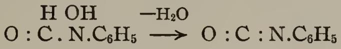
[1] Wieland: *Loc. cit.*

[2] Wieland: Die Knallsäure, p. 32 (1909).



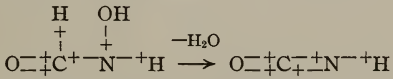
$$\overset{HH}{O : C}.N(OH) \xrightarrow{-H_2O} O : C : NH \xrightarrow{+H_2O} O : \overset{\substack{OH\\|}}{C}.NH_2 \longrightarrow CO_2 + NH_3$$

Biddle[1] found that the sodium salt and the lead salt of formhydroxamic acid could not be kept because they passed spontaneously into carbonates and ammonia. Bamberger and Destraz[2] subjected N-formylphenylhydroxylamine to the action of dehydrating agents (phosphorus pentoxide) and obtained phenyl isocyanate as one of the products of the action:



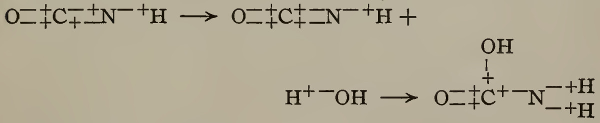
$$O : \overset{H}{C} . \overset{OH}{N}.C_6H_5 \xrightarrow{-H_2O} O : C : N.C_6H_5$$

If this change is assumed to proceed in a manner similar to those described in previous cases, that is, if the hydroxamic acid loses one molecule of water,[3] the isocyanate produced could not yield a carbamate or carbonate and ammonia without previous intramolecular oxidation, or exchange of electrons.



$$O\substack{-\\-}\substack{+\\+}\overset{\substack{H\\+\\|}}{C}{}^{+}{}^{-}\overset{\substack{OH\\|\\+}}{N}{}^{-}{}^{+}H \xrightarrow{-H_2O} O\substack{-\\-}\substack{+\\+}C\substack{-\\+}\substack{+\\-}N{}^{-}{}^{+}H$$

The electromere here represented must pass to a second electromere before carbamic acid or carbonic acid and ammonia can be formed:



$$O\substack{-\\-}\substack{+\\+}C\substack{-\\+}\substack{+\\-}N{}^{-}{}^{+}H \longrightarrow O\substack{-\\-}\substack{+\\+}C\substack{+\\+}\substack{-\\-}N{}^{-}{}^{+}H +$$

$$H^{+}{}^{-}OH \longrightarrow O\substack{-\\-}\substack{+\\+}\overset{\substack{OH\\|\\+}}{C}{}^{+}{}^{-}N\substack{-+H\\-+H}$$

Nitromethane, therefore, presents a very simple illustration

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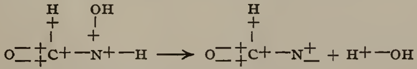
[1] Biddle: Ann. Chem. (Liebig), **310**, 15 (1899).

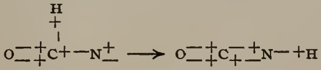
[2] Bamberger and Destraz: Ber. d. chem. Ges., **34**, 243 (1901); **35**, 1883 (1902).

[3] It may be assumed that a loss of one molecule of water yields first a univalent nitrogen derivative,



$$O\substack{-\\-}\substack{+\\+}\overset{\substack{H\\+\\|}}{C}{+}{-}\overset{\substack{OH\\|\\+}}{N}{+}{-}H \longrightarrow O\substack{-\\-}\substack{+\\+}\overset{\substack{H\\+\\|}}{C}{+}{-}N\substack{+\\-} + H{+}{-}OH$$

and that this undergoes rearrangement to give the isocyanate



$$O\substack{-\\-}\substack{+\\+}\overset{\substack{H\\+\\|}}{C}{+}{-}N\substack{+\\-} \longrightarrow O\substack{-\\-}\substack{+\\+}C\substack{-\\+}\substack{+\\-}N{-}{+}H$$

of the changes brought about by successive steps in the process of intramolecular oxidation and reduction. The initial and final stages may be summed up in a single equation:

$$CH_3NO_2 \longrightarrow CO_2 + NH_3$$

Therefore, starting with the carbon atom in the condition represented by the electronic symbol ${}^{-}_{-}C^{-}_{+}$ (or possibly ${}^{-}_{-}C^{-}_{-}$), the entire gamut of oxidation has been traversed, ending with the carbon atom in the condition shown by the symbol ${}^{+}_{+}C^{+}_{+}$, while, at the same time, the nitrogen atom has suffered reduction from the condition indicated by the symbol $N\begin{smallmatrix}+\\+\\+\\+\\-\end{smallmatrix}$ (or possibly $N\begin{smallmatrix}+\\+\\+\\+\\+\end{smallmatrix}$) to the state represented by the symbol $N\begin{smallmatrix}+\\-\\-\\-\\-\end{smallmatrix}$.

PART II. THE BECKMANN REARRANGEMENT

Now, the final stage in the change, viz., the change of formhydroxamic acid into isocyanic acid, is commonly classed among the Beckmann rearrangements. In my opinion, however, it is not essentially different in mechanism from any of the other changes which preceded it in the series. They all have, in common, intramolecular oxidation and reduction, or an exchange of negative electrons between the carbon atom and the nitrogen atom. In fact, if all of the reactions classed as examples of the Beckmann rearrangement (including the Hofmann and Curtius reactions) are inspected it will be observed *that in every case the rearrangement is accompanied by a process of intramolecular oxidation and reduction.* It seems very probable that this tendency of the system of linking carbon-nitrogen to pass to one in which the carbon atom is as fully oxidized as possible and the nitrogen atom as fully reduced as possible may be the real determining factor in the Beckmann rearrangement, and that the formation of univalent nitrogen, proposed by Stieglitz[1] as the immediate cause, may be a mere incident, necessary, to be sure, to pave the way for this change.

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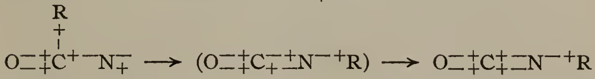
[1] Stieglitz: This Journal, **18**, 751 (1896); **28**, 49 (1903). Stieglitz and Earl: *Ibid.*, **30**, 399, 412 (1903). Stieglitz and Slossen: Ber. d. chem. Ges., **28**, 3266 (1896); **34**, 1613 (1902). Slossen: This Journal, **29**, 289 (1903). Jones: *Ibid.*, **48**, 1 (1912).

Univalent nitrogen may be represented by two electronic symbols:

$$^{+}\mathrm{N} \qquad\qquad ^{-}\mathrm{N}$$

In either case the two auxiliary valences (see p. 416) must be considered the one as positive ($^{+}$) and the other as negative ($^{-}$), since the loss of two groups from trivalent nitrogen necessitates that one be positive and the other negative. In the interpretation of the Beckmann rearrangement here proposed, this becomes a very significant fact. One of the free valences of univalent nitrogen must be positive ($^{+}$) in order that the carbon atom may be oxidized, that is, may lose negative electrons; and the other valence of univalent nitrogen must be negative ($^{-}$) to receive the positive radical (R^{+}) which can no longer remain attached to the carbon atom when all of its valences have become positive ($\overset{+}{\underset{+}{\mathrm{C}^{+}_{+}}}$). E. g.:



$$\mathrm{O}{}^{-+}_{-+}\overset{\mathrm{R}\atop{+\atop |}}{\mathrm{C}}{}^{+-}\mathrm{N}^{-}_{+} \longrightarrow (\mathrm{O}{}^{-+}_{-+}\mathrm{C}^{-}_{+}{}^{\pm}_{-}\mathrm{N}^{-+}\mathrm{R}) \longrightarrow \mathrm{O}{}^{-+}_{-+}\mathrm{C}^{+}_{+}{}_{-}\mathrm{N}^{-+}\mathrm{R}$$

Stieglitz[1] claims that the rearrangement is induced by the "potency of the free valences of univalent nitrogen." The present mode of viewing the rearrangement would speak rather of the "potency" of the carbon atom to lose negative electrons and of the nitrogen atom to acquire them, and would look upon the free valences of univalent nitrogen as the stage setting required to furnish a suitable environment in which the essential action may take place.

The following classes of compounds include those usually discussed in connection with the Beckmann rearrangement: β-monosubstituted hydroxylamines, RNHOH; bromoamines, RNHBr; alphyl azides, $\mathrm{R.CH_2.N_3}$; aldoximes, RCH:NOH; ketoximes, RRC : NOH; hydroxamic acids RC(: O).N(OH)H and their mono- and diacyl derivatives; alkyl esters of hydroximic acids, RC(OR) : NOH; amidoximes, $\mathrm{RC(NH)_2}$:NOH; acid azides, $\mathrm{RC(:O).N_3}$; and monohalogen amides, RC(: O).N(hal)H. The view of the Beckmann rearrangement presented above would lead naturally to a classification of organic compounds into groups determined by the state of oxidation which the carbon atom attached to nitrogen shows preceding and subsequent to the rearrangement. It will be pointed out that in all of these types of compounds, including the monohalogen amines, the monohalogen amides and the azides, the nitrogen atom is actually or potentially[1] in a state of oxidation corresponding to that which it has in hydroxylamine, and that it passes during rearrangement to a state of oxidation comparable to that which nitrogen has in ammonia. In accordance with these principles there would be three distinct groups:

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[1] Stieglitz: *Loc. cit.*

Group I.—Compounds in which the carbon atom of the carbon-nitrogen linking may be regarded as having the state of oxidation shown by the carbon atom in methyl alcohol. During rearrangement the state of oxidation is changed to that shown by the carbon atom in formaldehyde. These changes may be illustrated by the following symbols:

$$\underset{\text{(Alcohol)}}{\mathrm{C}\substack{-\\-\\-\\+}} \quad \text{and} \quad \underset{\substack{\text{(Hydroxyl-}\\\text{amine)}}}{\mathrm{N}\substack{-\\-\\+}} \quad \xrightarrow[\text{to}]{\text{rearrange}} \quad \underset{\substack{\text{(Aldehyde}\\\text{or ketone)}}}{\mathrm{C}\substack{-\\-\\+\\+}} \quad \text{and} \quad \underset{\text{(Ammonia)}}{\mathrm{N}\substack{-\\-\\-}}$$

Group II.—Compounds in which the carbon atom of the carbon-nitrogen linking is in a state of oxidation corresponding to that of the carbon atom in formaldehyde. By rearrangement it passes to a state of oxidation comparable to that of the carbon atom in formic acid:

$$\underset{\substack{\text{(Aldehyde}\\\text{or ketone)}}}{\mathrm{C}\substack{-\\-\\+\\+}} \quad \text{and} \quad \underset{\substack{\text{(Hydroxyl-}\\\text{amine)}}}{\mathrm{N}\substack{-\\-\\+}} \quad \xrightarrow[\text{to}]{\text{rearrange}} \quad \underset{\text{(Acid)}}{\mathrm{C}\substack{-\\+\\+\\+}} \quad \text{and} \quad \underset{\text{(Ammonia)}}{\mathrm{N}\substack{-\\-\\-}}$$

Group III.—Compounds in which the carbon atom of the carbon-nitrogen linking is in a state of oxidation shown by the carbon atom in formic acid. By rearrangement the state of oxidation changes to that shown by the carbon atom in carbonic acid:

$$\underset{\text{(Acid)}}{\mathrm{C}\substack{-\\+\\+\\+}} \quad \text{and} \quad \underset{\text{(Hydroxylamine)}}{\mathrm{N}\substack{-\\-\\+}} \quad \xrightarrow[\text{to}]{\text{rearrange}} \quad \underset{\text{(Carbonic acid)}}{\mathrm{C}\substack{+\\+\\+\\+}} \quad \text{and} \quad \underset{\text{(Ammonia)}}{\mathrm{N}\substack{-\\-\\-}}$$

[1] Jones: THIS JOURNAL, **48**, 26 (1912).

Group I would include azides, such as benzyl azide,[1] $C_6H_5.CH_2.N_3$; monosubstituted hydroxylamines, such as triphenylmethylhydroxylamine,[2] $(C_6H_5)_3C.N(OH)H$; and monobromo amines, such as triphenylamine bromide,[3] $(C_6H_5)_3C.NH(Br)$. Group II would include aldoximes and ketoximes. Group III would include hydroxamic acids, together with their salts and esters, amidoximes, acid azides and monohalogenamides.[4]

Much speculation has been indulged in to explain the manner in which the radical, R, attached to the carbon atom "wanders" to the nitrogen atom. Apart from the plain proposal that the radical, as a whole, changes its position without any complicated mechanism, several hypotheses, involving a change in the character of the radical, have been advanced, but none has satisfied the demands placed upon it by experiment. Hesse[5] showed that intermediate trimethylene rings could not be assumed since trimethylacetbromoamide, $(CH_3)_3CONHBr$, gave tertiary butylamine by rearrangement, while the assumption of the intermediate formation of a trimethylene ring would require isobutylamine. Nef proposed that the dissociation into bivalent carbon radicals might precede the rearrangement. The evidence for and against this view has been presented by Stieglitz.[6] At present it cannot be regarded as a satisfactory interpretation. It must be admitted, therefore, that we have no satisfactory mechanism in terms of which to represent the "wandering" of the radical from the carbon atom to the nitrogen atom. The difficulties met with in the rearrangement of stereoisomers are also awaiting explanation. Work is now in progress in this laboratory which promises to throw new light upon these phases of the Beckmann rearrangement.

UNIVERSITY OF CINCINNATI
November 11, 1913

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[1] Curtius: J. prakt. Chem., [2] **50**, 289; Ber. d. chem. Ges., **27**, 778 (1895).

[2] Stieglitz and Leech: Ber. d. chem. Ges., **46**, 2147 (1913).

[3] Stieglitz and Vosburgh: *Ibid.*, **46**, 2151 (1913).

[4] Jones: THIS JOURNAL, **48**, 26 (1912).

[5] Stieglitz: *Ibid.*, **29**, 56 (1903).

[6] Stieglitz: *Ibid.*, p. 57.

[Contribution from the Chemical Laboratory of the University of Cincinnati]

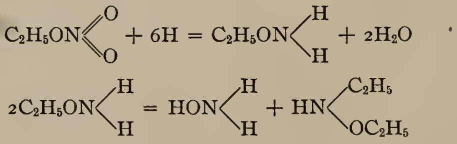
A STUDY OF SOME NEW ALKYLHYDROXYLAMINES

By Charles H. Hecker

The amines have never ceased to be a center of interest since the time of their discovery by Wurtz in 1848. Although substituted hydroxylamines are nearer akin to amines than to any other class of organic compounds, they have shared only to a very minor degree in the attention paid to organic derivatives of nitrogen. Still, in many ways, the questions raised by a deductive consideration of their chemical relations are somewhat more varied and interesting than those presented by amines themselves. The present study, carried out under the direction of Dr. Lauder W. Jones, had, for its main object, the finding of methods whereby the various alkyl derivatives of hydroxylamine may be prepared in sufficient quantities and with a degree of readiness to permit of their future investigation from many other angles. Preliminary arrangements have already been made to study the electrical conductivities of water solutions of the alkylhydroxylamines described in this article.

HISTORICAL

The first representative of the alkylhydroxylamines[1] was described in 1868 by Lossen,[2] the discoverer of hydroxylamine itself. He found that one of the products of the reduction of ethyl nitrate by tin and hydrochloric acid was a base having the formula $C_4H_{11}ON$. Its properties showed that it was related to hydroxylamine, and he concluded that it was ethoxyethylamine, assuming that the following reactions took place:



$$C_2H_5ON\Big\langle\begin{matrix}O\\O\end{matrix} + 6H = C_2H_5ON\Big\langle\begin{matrix}H\\H\end{matrix} + 2H_2O$$

$$2C_2H_5ON\Big\langle\begin{matrix}H\\H\end{matrix} = HON\Big\langle\begin{matrix}H\\H\end{matrix} + HN\Big\langle\begin{matrix}C_2H_5\\OC_2H_5\end{matrix}$$

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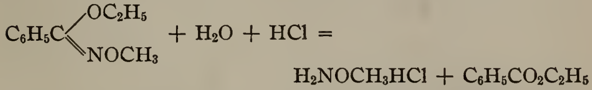
[1] Vorländer: J. prakt. Chem., N. F., **59**, 247–8. Throughout this paper the terms "alkyl" and "alphyl" are used interchangeably.

[2] Lossen: Ann. Chem. (Liebig), Suppl. **6**, 238.

Later, however, Lossen[1] showed that this compound was not ethoxyethylamine, neither is it identical with β-diethylhydroxylamine. Its constitution is doubtful.

No further study of either hydroxylamine or its derivatives was made until, in 1875, Lossen endeavored to justify the formula of hydroxylamine $\left(HON\langle{}^{H}_{H}\right)$, which had been criticized, by showing that two of the hydrogen atoms were equivalent, while the third was not. To do this, he replaced these hydrogen atoms by different groups, principally acyl groups.

The next year, Lossen and Zanni[2] prepared the hydrochloride of α-methylhydroxylamine by hydrolyzing the methyl ester of ethylbenzhydroximic acid, as shown by the equation



$$C_6H_5C\begin{matrix}\diagup OC_2H_5\\ \diagdown NOCH_3\end{matrix} + H_2O + HCl = H_2NOCH_3HCl + C_6H_5CO_2C_2H_5$$

but they did not isolate the alkylhydroxylamine itself. Petraczek[3] obtained the same substance by hydrolyzing methylbenzaldoxime with concentrated hydrochloric acid:

$$C_6H_5CH:N.OCH_3 + H_2O + HCl = C_6H_5CHO + H_2NOCH_3HCl$$

Jones[4] also obtained this substance by hydrolyzing the α-methyl ester of carbethoxyhydroxamic acid with hydrochloric acid.

Lossen and Zanni made α-ethylhydroxylamine by a hydrolysis similar to that given above. Later Waldstein[5] prepared it from benzhydroxamic ethyl ester by heating this substance with an excess of hydrochloric acid in a sealed tube. Jones[6] obtained the hydrochloride by treating the reaction product of phosphorus pentachloride and carbethoxyhydroxamic ethyl ester with water, making this solution strongly alkaline with sodium hydroxide and distilling the hydroxylamine into dilute hydrochloric acid. This method gives almost theoretical yields. α,β-Dimethylhydroxylamine and α,β-diethylhydroxylamine,[1] also α-methyl-β-ethylhydroxylamine and α-ethyl-β-methylhydroxylamine,[2] were obtained by Jones by hydrolyzing the respective esters of carbethoxyhydroxamic acid. Lossen had previously obtained the diethylhydroxylamine by alkylating α-ethylhydroxylamine with ethyl bromide.[3]

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[1] Lossen: Ann. Chem. (Liebig), **252**, 234.

[2] Lossen and Zanni: *Ibid.*, **182**, 225ff.

[3] Petraczek: Ber. d. chem. Ges., **16**, 827.

[4] Jones: THIS JOURNAL, **20**, 41ff.

[5] Waldstein: Ann. Chem. (Liebig), **181**, 390

[6] Jones: THIS JOURNAL, **20**, 41ff.

In 1888, Bewad[4] thought that he had made triethylamine oxide $(C_2H_5)_3NO$, by the action of nitroethane upon zinc ethyl, but this compound was shown later[5] to be β-ethyl-β-sec.-butylhydroxylamine. This synthesis furnishes an easy way of preparing mixed β,β-dialkylhydroxylamines, and was extensively studied by Bewad.[6]

In 1890, Behrend and Leuchs[7] published a résumé of the work done on the alkyl derivatives of hydroxylamine up to that time, and presented the results of their own investigations in that field, covering the benzyl and ethyl derivatives. Nine years later Dunstan and Goulding[8] in England, and Mamlock and Wolffenstein[9] in Germany, by the oxidation of di- and trisubstituted amines with hydrogen peroxide obtained a number of β-dialkylhydroxylamines and the so-called oxamines, or hydroxyamine oxides, compounds isomeric with the trialkylhydroxylamines.

Summing up, we see that up to the present time there is only a single representative of the α-monoalkylhydroxylamines known, for although Lossen and Zanni obtained the hydrochloride of α-methylhydroxylamine, they did not isolate the base. There is a similar paucity of data on the α,β-dialkylhydroxylamines, only two compounds containing like groups and two compounds containing unlike groups being known.

In the present paper are described two new α-monoalkylhydroxylamines, six new α,β-dialkylhydroxylamines, and the intermediate products in their preparation, many of which are new. Four of these dialkylhydroxylamines are isomeric with each other and with the β,β-ethylpropylhydroxylamine described by Bewad. It is intended to study all of these compounds and others, including the sixth isomer, β-ethyl-β-isopropylhydroxylamine, yet to be made, from the standpoint of their electrical conductivities in water solution.

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[1] Jones: This Journal, **20**, 41ff.

[2] Jones: *Ibid.*, **38**, 253ff.

[3] Lossen: Ann. Chem. (Liebig), **252**, 234.

[4] Bewad: Ber. d. chem. Ges., **21**, Ref. 479.

[5] Bewad: J. Russ. Phys. Chem. Soc., **32**, 455.

[6] Bewad: J. prakt. Chem., N. F., **63**, 94ff. and 193ff.

[7] Behrend and Leuchs: Ann. Chem. (Liebig), **257**, 203ff.

[8] Dunstan and Goulding: J. Chem. Soc., **75**, 799ff., 1004ff.

[9] Mamlock and Wolffenstein: Ber. d. chem. Ges., **33**, 159.

The method suggested by Jones[1] of introducing successively into hydroxyurethan two different alkyl groups and subsequently hydrolyzing the resulting product was followed in the preparation of the α,β-dialkylhydroxylamines. An alcoholic solution of hydroxyurethan mixed with the theoretical amount of alkyl halide was treated with the calculated amount of an alcoholic solution of potassium hydroxide. This formed a mixture of the mono- and dialkyl esters of carbethoxyhydroxamic acid. One might expect that some of the oxygen ester ($C_2H_5O.C(OR) : NOR$) would be formed at the same time, but none was observed. These two substances were then separated by shaking the ether solution with dilute alkali. By this treatment, the monoalkyl derivative was converted into its salt, which dissolved in the water, while the dialkyl derivative, having no acid properties, remained dissolved in the ether. The alkali salt of the monoalkyloxyurethan was easily decomposed by dilute acids to give the free ester, which was extracted with ether, and then obtained in the free state by fractional distillation.

When a mixed α,β-dialkylhydroxylamine was to be made, a mixture of one mole of monoalkylcarbethoxyhydroxamic ester and one mole of alkyl halide was treated with the calculated amount of sodium ethylate dissolved in alcohol. After the dialkyl ester was extracted with ether, it was shaken with dilute alkali to remove any unchanged monoalkyl ester, then dried and fractionated.

The hydrolysis of these esters was accomplished uniformly by heating the ester with a considerable excess of potassium hydroxide solution in a sealed tube for fifteen to sixty hours at temperatures varying from 100° to 200°. To separate the hydroxylamine, the mixture from the hydrolysis was distilled and the free base collected in dilute hydrochloric acid. The hydrochloride formed was recrystallized, decomposed with potassium hydroxide and the vapors of the free alkylhydroxylamine condensed.

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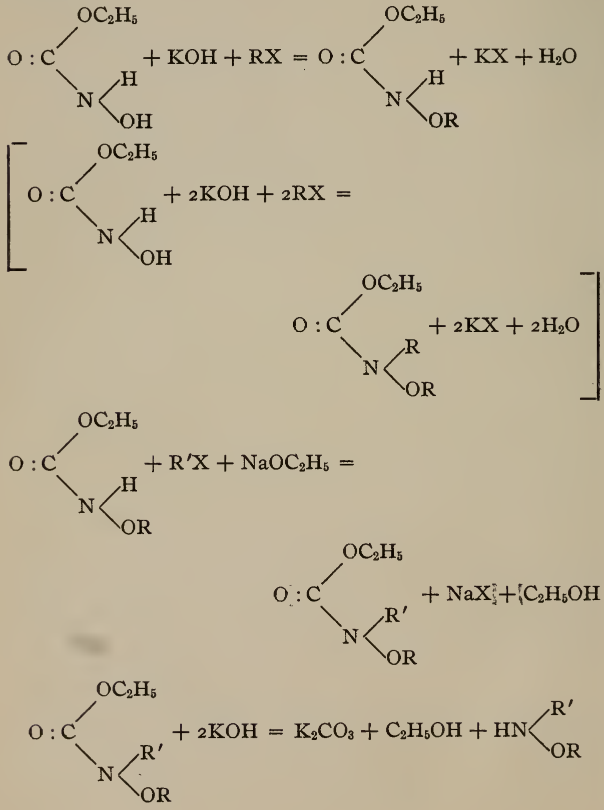
[1] Jones: This Journal, **38**, 253ff.

The above method may be summarized in the following equations:

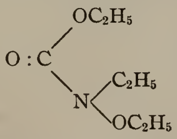


Concentrated hydrochloric acid was tried as the hydrolyzing agent, but gave poor yields of a very impure salt. The α-monoalkyl esters were easily hydrolyzed by the potassium hydroxide solution, but the dialkyl esters with two like groups were decomposed much more slowly. Furthermore, the ease with which the α-monoalkyl esters were hydrolyzed seemed to increase with increasing molecular weight. This is probably partly responsible for the low yields obtained in making the α-monoalkyl esters of carbethoxyhydroxamic acid.

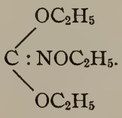
EXPERIMENTAL PART

Action of Ethyl Iodide on the Potassium Salt of Carbethoxyhydroxamic Acid

The carbethoxyhydroxamic acid, which served as the starting point in the preparation of the following compounds, was prepared according to Jones's modification of Hantzsch's method.[1] This was then converted into the ethyl ester by treatment with ethyl iodide and potassium hydroxide,[2] and the mono- and di-esters separated as described above. The monoethyl ester was used in the preparation of mixed dialkylcarbethoxyhydroxamic esters. The ether solution of the diethyl ester was dried with anhydrous sodium sulphate and the ether was removed by distillation, under diminished pressure. The oil which was left was impure, as was that obtained by Jones. It was, therefore, fractionated, and two approximately equal fractions, one boiling at 107° to 112° (70 mm. pressure) and the other boiling at 129° to 133° (70 mm. pressure) were obtained. It was at first thought that these two fractions might be two tautomeric forms, viz.:



and



This could, of course, be determined easily, for the first should give α-diethylhydroxylamine on hydrolysis with potassium hydroxide, while the second should give α-monoethylhydroxylamine. However, the nature of the impurity was determined without this step. An analysis of the higher boiling fraction gave the following results:

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[1] Jones: THIS JOURNAL, **20**, 41ff.

[2] *Ibid.*

0.3987 gram gave 39.2 cc. N_2 at 21° and 747.8 mm. (uncorr.).

	Calc. for α-diethyloxyurethan $C_7H_{15}O_3N$	Calc. for α-monoethyloxyurethan $C_5H_{11}O_3N$	Found
N	8.69	10.52	10.95

The boiling point of this fraction was found to be 194° to 196° under 750 mm. pressure. The boiling point of α-monoethylcarbethoxyhydroxamic ester is 195° to 196°.[1]

The following results were obtained from an analysis of the other fraction:

0.2258 gram gave 0.4299 gram CO_2 and 0.1873 gram H_2O.

	Calc. for $C_7H_{15}O_3N$	Found
C	52.11	52.00
H	9.39	9.29

From this it is seen that the impurity which contaminated the neutral portion obtained from the action of ethyl iodide upon the potassium salt of carbethoxyhydroxamic acid was α-ethylcarbethoxyhydroxamic ester.

Action of Ethyl Iodide on α-Ethylcarbethoxyhydroxamic Ester

An alcoholic solution containing the theoretical amount of sodium ethylate was gradually added to a mixture of 14 grams of α-ethylcarbethoxyhydroxamic ester and 16.4 grams of ethyl iodide. The mixture grew warm and sodium iodide soon began to crystallize. After standing at room temperature for two days, the mixture was heated on the water bath at 80° for two hours. Most of the alcohol was then removed by distillation and the residue filtered from the dense precipitate of sodium iodide. The solution was then diluted with water, and extracted repeatedly with ether. The ether solution was shaken several times with dilute alkali to remove unchanged α-ethylcarbethoxyhydroxamic ester, dried with anhydrous sodium sulphate and fractionated. Twelve and one-half grams of the diethyl ester, boiling at 72°–74° under 12 mm. pressure, were obtained. The yield was 76 per cent. of the theoretical. The oil prepared in this way was identical in every respect with that obtained as the by-product in ethylating hydroxyurethan with ethyl iodide and potassium hydroxide.

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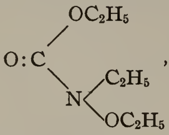
[1] Jones: This Journal, **20**, 41ff.

α-Diethylcarbethoxyhydroxamic ester,  $O:C\begin{matrix}OC_2H_5\\ N\begin{matrix}C_2H_5\\ OC_2H_5\end{matrix}\end{matrix}$, is a colorless oil, with a disagreeable odor suggesting an isocyanide. It is very slightly soluble in water, and is soluble in all proportions in alcohol and ether. It gives no color test with ferric chloride, and does not reduce ammoniacal silver nitrate or Fehling's solution.

Decomposition of α-Diethylcarbethoxyhydroxamic Ester with Potassium Hydroxide

A mixture of 12.5 grams of the diethyl ester and 20 grams of potassium hydroxide dissolved in water was heated together in a sealed tube at 100° for 30 hours. The contents of the tube were then distilled, and the distillate passed into a dilute solution of hydrochloric acid. Since the distillate did not all dissolve in the hydrochloric acid, the solution was extracted with ether. Five grams of the undecomposed ester were recovered from the ether by fractionation. The acidified distillate was concentrated on the water bath and the last portions of water and hydrochloric acid were removed by placing the thick liquid in a vacuum desiccator containing concentrated sulphuric acid and pieces of solid potassium hydroxide. After some time the liquid had solidified to a mass of white crystals. identical with those obtained by Jones.[1] The free base can be obtained by heating a mixture of the dry salt and potassium hydroxide. It was first prepared by Lossen[2] from the oxalate, and was fully described by him.

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[1] Jones: THIS JOURNAL, **20**, 41ff.

[2] Lossen: Ann. Chem. (Liebig), **252**, 234.

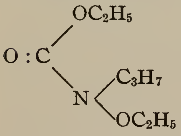
I. α-Ethyl-β-propylhydroxylamine

(*a*) *Action of Normal Propyl Iodide on α-Ethylcarbethoxyhydroxamic Ester.*—The action of a mixture of normal propyl iodide and sodium ethylate upon α-ethylcarbethoxyhydroxamic ester proceeds very slowly in the cold, but quite rapidly at higher temperatures. Thus, a solution of 35.5 grams of α-ethylcarbethoxyhydroxamic ester, 45.5 grams of normal propyl iodide and the theoretical amount of sodium ethylate in absolute alcohol gave a slight precipitate of sodium iodide after standing at room temperature for four days. The precipitate was filtered from the solution, and this was then heated on the water bath at 80° for half an hour. A dense precipitate formed, which was removed. After the solution had been diluted with water, it was extracted a number of times with ether. The little free iodine which was present was removed with sodium thiosulphate, the ether solution was dried and 33 grams of the α-ethyl-β-propylcarbethoxyhydroxamic ester were obtained by fractionation. The yield was 71 per cent. of the theoretical.

0.4076 gram gave 29 cc. N_2 at 18° and 750 mm. (uncorr.).

	Calc. for $C_8H_{17}O_3N$	Found
N	8.00	8.11

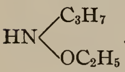
α-Ethyl-β-propylcarbethoxyhydroxamic ester,



$$O:C\begin{cases}OC_2H_5\\ N\begin{cases}C_3H_7\\ OC_2H_5\end{cases}\end{cases}$$

, is a colorless oil boiling at 189° under 740 mm. pressure. It has an odor similar to nicotine, and is soluble in water, alcohol and ether. It gives no reaction with ferric chloride, ammoniacal silver nitrate or Fehling's solution.

(*b*) *Preparation of α-Ethyl-β-propylhydroxylamine*,



$$HN\begin{cases}C_3H_7\\ OC_2H_5\end{cases}$$

.—The hydrolysis of the corresponding ester of carbethoxyhydroxamic acid was accomplished most easily as follows: Fifteen grams of the ester, mixed with an aqueous solution containing 30 grams of potassium hydroxide, were heated in a sealed tube at about 120° for twenty-four hours. The product from the hydrolysis was then treated in the same way as described under α-diethylcarbethoxyhydroxamic ester (see page 451).

α-Ethyl-β-propylhydroxylamine hydrochloride crystallizes in large plates melting at 72°.5–73°. This salt is easily soluble in alcohol, benzene, chloroform and toluene. It is not soluble in ether and very slightly soluble in carbon bisulphide. An alcoholic solution of platinic chloride with an alcoholic solution of the hydrochloride gave a solution of the chloroplatinate. By the addition of dry ether to the solution the salt was precipitated as brilliant, deep yellow crystals, which melted at 150°.2.

0.2490 gram gave 0.0794 gram platinum.

	Calc. for $C_{10}H_{28}O_2N_2PtCl_6$	Found
Pt	32.19	31.88

To prepare α-ethyl-β-propylhydroxylamine, the hydrochloride was distilled with an excess of concentrated sodium hydroxide solution, and the vapors passed over pieces of solid sodium hydroxide heated to 95° before they were condensed. It is a clear, colorless liquid boiling at 83°.8–84° and has a sharp ammoniacal odor and a sweet, biting taste. It reduces ammoniacal silver nitrate solution slowly in the cold, and very rapidly when warmed. It does not reduce Fehling's solution in the cold, but does so slowly on being heated. It gives no color reaction with ferric chloride. It is slightly soluble in water, and is soluble in all proportions in alcohol. Its specific gravity is 0.8033 (25°/25°). Its index of refraction at 25° is 1.39426.

II. α-Ethyl-β-isopropylhydroxylamine

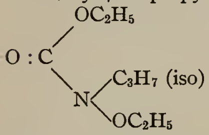
(*a*) *Action of Isopropyl Iodide and Sodium Ethylate on α-Ethylcarbethoxyhydroxamic Ester*

Isopropyl iodide reacts with α-ethylcarbethoxyhydroxamic ester in the presence of sodium ethylate just as its isomer does. Thus, 28 grams of the α-ethyl ester of carbethoxyhydroxamic acid and 36 grams of isopropyl iodide, when treated with the calculated amount of sodium ethylate dissolved in alcohol, gave a fine, white precipitate of sodium iodide after standing for several days at room temperature. This precipitation was hastened by warming the solution on the water bath. The alcoholic solution was filtered, diluted with water and extracted with ether. The ether solution was then shaken with dilute potassium hydroxide solution, dried and fractionated. Twenty-four grams of α-ethyl-β-isopropylhydroxamic ester were obtained. The yield was 66 per cent. of that required by theory.

0.3015 gram gave 23 cc. N_2 at 24° and 739 mm. pressure (uncorr.).

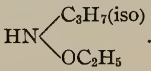
	Calc. for $C_8H_{17}O_3N$	Found
N	8.00	8.27

α-Ethyl-β-isopropylcarbethoxyhydroxamic ester,



, is a clear, colorless oil boiling at 182° under 748 mm. pressure (84°–87° under 14–15 mm.). It has a strong odor resembling parsnips. Its aqueous solution does not reduce ammoniacal silver nitrate, and gives no coloration with ferric chloride.

(*b*) *Preparation of α-Ethyl-β-isopropylhydroxylamine,*



$$HN\left\langle\begin{array}{l}C_3H_7(iso)\\OC_2H_5\end{array}\right..$$

A mixture of 15 grams of α-ethyl-β-isopropylcarbethoxyhydroxamic ester and 25 grams of potassium hydroxide dissolved in water were heated in a sealed tube at 120°–160° for 36 hours. The aqueous solution of the free base, thus formed, was distilled, and the distillate passed into dilute hydrochloric acid. All of the ester had been hydrolyzed. Another tube, charged in the same way and heated to 110° for forty hours, gave five grams of unhydrolyzed ester on extraction of the acidified distillate with ether. The solution of the hydrochloride was concentrated by evaporation on the water bath, and then placed in a vacuum desiccator containing concentrated sulphuric acid and potassium hydroxide. The salt had not crystallized from the liquid after one month, so the liquid was placed in a vacuum desiccator over phosphorus pentoxide and kept at room temperature for one week, then at 0° for a week. By this treatment a syrupy liquid, intermixed with a few tiny crystals (probably ammonium chloride), was obtained. A mixture of 3 grams of this syrupy hydrochloride with 6 grams of powdered potassium hydroxide was dry distilled and gave 1.90 grams of the free base.

α-Ethyl-β-isopropylhydroxylamine is a clear, colorless liquid boiling at 78°. It has an odor very much like that of ethylamine. Its specific gravity (25°/25°) is 0.8132. The base is soluble in a large amount of water and this solution does not reduce ammoniacal silver nitrate in the cold, but does so rapidly when warmed. It does not reduce Fehling's solution when hot or cold.

An alcoholic solution of platinic chloride precipitated the chloroplatinate from a hot alcoholic solution of the hydrochloride as small lemon-yellow crystals. These decomposed without melting when heated.

0.2060 gram gave 0.0660 gram Pt.

	Calc. for $C_{10}H_{28}O_2N_2PtCl_6$	Found
Pt	32.19	32.04

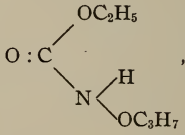
III. *α-Propylhydroxylamine*, $H_2NOC_3H_7$

(*a*) *Action of Normal Propyl Iodide on the Potassium Salt of Hydroxyurethan.*—When an alcoholic solution containing 33.6 grams of potassium hydroxide was slowly added, with constant shaking, to a mixture of 64 grams of normal propyl bromide, 13.6 grams of normal propyl iodide and 63 grams of hydroxyurethan, the mixture became turbid and the temperature rose slightly. The flask was, therefore, cooled to prevent, as far as possible, the hydrolysis of the mono ester by the potassium hydroxide. After standing for a week at room temperature, the mixture was heated for one-half hour at 80°. The salt which had precipitated was removed by filtration, most of the alcohol was distilled off, the remaining solution was diluted with water and extracted repeatedly with ether. The ether solution was then shaken with the calculated amount of a dilute solution of potassium hydroxide. The ether solution which was left contained the dipropylcarbethoxyhydroxamic ester (see below), and the water solution contained the monopropylcarbethoxyhydroxamic ester in the form of the potassium salt. To obtain the free ester, the alkaline solution was acidified with 10 per cent sulphuric acid, and extracted with ether. The ether solution was colored by a little free iodine, which was removed with sodium thiosulphate solution. The ether solution was dried and then fractionated under diminished pressure, since the ester decomposes somewhat when distilled under atmospheric pressure. The yield was 32 grams, only 36.3 per cent. of the theoretical yield.

0.3119 gram gave 28.3 cc. N_2 at 23°.5 and 733.8 mm.

	Calc. for $C_6H_{13}O_3N$	Found
N	9.55	9.84

α-Propylcarbethoxyhydroxamic ester,



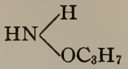
$O:C(OC_2H_5)N(H)(OC_3H_7)$

, is a colorless oil boiling at 109°–111° under 15 mm. pressure. At atmospheric pressure it boils between 200° and 210° with slight decomposition. It is not appreciably soluble in water, but is soluble in all proportions in alcohol and in ether. It has a faint, pleasant odor.

The ether solution of the dipropylcarbethoxyhydroxamic ester (see above) was dried with anhydrous sodium sulphate and fractionated. Nine and one-half grams (8.5 per cent. of the theoretical) of dipropylcarbethoxyhydroxamic ester were obtained. It is a clear, colorless oil, insoluble in water, boiling at 107°.5–108° under 20 mm. pressure. It has an odor resembling roasted chestnuts.

0.3192 gram gave 23 cc. N_2 at 22° and 740 mm. pressure.

	Calc. for $C_9H_{19}O_3N$	Found
N	7.40	7.80

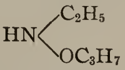
(*b*) *Preparation of α-Propylhydroxylamine,*  $\mathrm{HN}\left\langle\begin{matrix}\mathrm{H}\\ \mathrm{OC_3H_7}\end{matrix}\right.$.—

Ten grams of α-propylcarbethoxyhydroxamic ester and 20 grams of potassium hydroxide dissolved in water formed a homogeneous mixture. This mixture was heated in a sealed tube at 100° for 12 hours. The resulting products from the hydrolysis were distilled and the distillate collected in dilute hydrochloric acid. This was concentrated by evaporation on the water bath, and then placed in a vacuum desiccator containing concentrated sulphuric acid and solid potassium hydroxide. α-Propylhydroxylamine hydrochloride crystallized from the solution in large, thin, transparent white plates, which melted at 140°–141°. The salt is very soluble in water and in alcohol, but insoluble in ether. It is not deliquescent. An alcoholic solution of platinic chloride precipitated the chloroplatinate as light yellow crystals from an alcoholic solution of the hydrochloride.

0.1103 gram gave 0.0408 gram Pt.

	Calc. for $(C_3H_{10}ON)_2PtCl_6$	Found
Pt	35.48	36.89

When a mixture of 2.67 grams of α-propylhydroxylamine hydrochloride and 6 grams of finely powdered potassium hydroxide was subjected to dry distillation, 1.35 grams of a clear, colorless liquid, having a sweetish, ammoniacal odor, were obtained. The yield was 75 per cent. of the theoretical. α-Propylhydroxylamine boils at 86°.6–87°. Its specific gravity (25°/25°) is 0.8687. Its aqueous solution rapidly reduces ammoniacal silver nitrate and Fehling's solution in the cold.

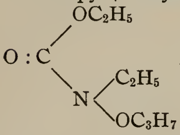
IV. α-Propyl-β-ethylhydroxylamine,  $\mathrm{HN}\left\langle\begin{matrix}\mathrm{C_2H_5}\\ \mathrm{OC_3H_7}\end{matrix}\right.$

(*a*) *Action of Ethyl Iodide on α-Propylcarbethoxyhydroxamic Ester.*—Five grams of sodium dissolved in alcohol were slowly added to an alcoholic solution containing 32 grams of α-propylcarbethoxyhydroxamic ester and 35 grams of ethyl iodide. The mixture was allowed to stand at room temperature for a week, and was then heated to 70° for four hours to complete the reaction. Most of the alcohol was then distilled off, the solution was diluted with water and extracted with ether. The ether extract was shaken with dilute potassium hydroxide solution to remove free iodine and any unchanged monopropyl ester present, then dried with sodium sulphate. After a few hours, the solution became dark brown, due to free iodine. Repeated shaking with sodium thiosulphate solution was necessary to remove all of the color. The solution was again dried and fractionated under 750 mm. pressure. Thirty grams of α-propyl-β-ethylcarbethoxyhydroxamic ester were obtained. The yield was 79 per cent. of the theoretical.

0.3512 gram gave 27 cc. N_2 at 27° and 750.4 mm. pressure.

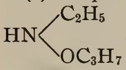
	Calc. for $C_8H_{17}O_3N$	Found
N	8.00	8.33

α-Propyl-β-ethylcarbethoxyhydroxamic ester,



, is a colorless liquid which boils at 191° under 750 mm. pressure without decomposition (92°.5 under 20 mm.). It has an odor similar to α,β-diethylcarbethoxyhydroxamic ester. It is not soluble in water, but is very soluble in alcohol and in ether.

(*b*) *Preparation of α-Propyl-β-ethylhydroxylamine*,



.—A mixture of 10 grams of α-propyl-β-ethylcarbethoxyhydroxamic ester and 20 grams of potassium hydroxide dissolved in water was heated in a sealed tube at 130° for 24 hours. The contents of the tube were then treated in the customary manner, and the hydrochloric acid solution extracted with ether. One-half gram of unhydrolyzed ester was recovered from the ether extract. The acid solution was concentrated on the water bath. During this operation considerable α-propyl-β-ethylhydroxylamine hydrochloride was lost by volatilization. Only 1.7 grams of α-propyl-β-ethylhydroxylamine hydrochloride was obtained. This was purified by precipitation with ether from an alcoholic solution. It forms large, lustrous crystals, resembling benzoic acid in appearance, which melt without decomposition at 96°.2. It is moderately soluble in cold chloroform and readily soluble in boiling chloroform, from which it crystallizes on cooling. It is very deliquescent. Its aqueous solution does not reduce ammoniacal silver nitrate or Fehling's solution, either cold or hot. An alcoholic solution of platinic chloride precipitated the chloroplatinate from an alcoholic solution of the hydrochloride as small, light yellow crystals, which decomposed when melted.

When 1.14 grams of the hydrochloride were mixed with 4 grams of finely powdered potassium hydroxide and distilled, 0.31 gram of a clear, colorless liquid, having an odor similar to its isomer, was obtained. α-Propyl-β-ethylhydroxylamine is moderately soluble in water, and this solution reduces ammoniacal silver nitrate slowly in the cold and rapidly on warming. It does not reduce Fehling's solution either hot or cold. The free base is very volatile.

V. α-*Dipropylhydroxylamine*

(*a*) *Hydrolysis of* α,β-*Dipropylcarbethoxyhydroxamic Ester.*—Fifteen grams of dipropylcarbethoxyhydroxamic ester and 20 grams of potassium hydroxide were heated together in a sealed tube at 130° for 40 hours. The contents of the tube were then treated in the usual way, and the hydrochloride of α-dipropylhydroxylamine obtained as white crystals, mixed with a little ammonium chloride. The salt was easily purified by dissolving the impure product in absolute alcohol, filtering from the ammonium chloride, and then adding absolute ether. This precipitated the salt as small, lustrous crystals, which melted at 146°.6. These crystals were extremely soluble in water but were not at all deliquescent. When an alcoholic solution of platinic chloride was added to an alcoholic solution of the hydrochloride, deep yellow crystals of the chloroplatinate were precipitated.

0.1634 gram gave 0.0498 gram Pt.

	Calc. for $C_{12}H_{32}O_2N_2PtCl_6$	Found
Pt	30.29	30.47

By distillation of 3 grams of the hydrochloride with finely powdered potassium hydroxide, 1.76 grams of α,β-propylhydroxylamine were obtained. The yield is 77 per cent. of the theoretical. It is a clear, colorless liquid boiling at 85°–86°. Its specific gravity (25°/25°) is 0.8141. It is somewhat soluble in water, and this solution instantly reduces ammoniacal silver nitrate solution in the cold, but has no effect upon Fehling's solution even when boiled with it.

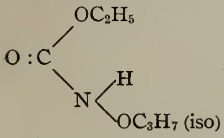
VI. α-Isopropylhydroxylamine

(*a*) *Action of Isopropyl Halides on the Potassium Salt of Carbethoxyhydroxamic Acid.*—Isopropyl halides react with difficulty with the sodium and potassium salts of carbethoxyhydroxamic acid. When the usual method for carrying out the reaction between isopropyl halides and carbethoxyhydroxamic acid in the presence of potassium hydroxide was tried, it was found impossible to increase the yield of the monoisopropylcarbethoxyhydroxamic ester much above 20 per cent. Usually the yield was lower than this. The following data represent an average experiment: Thirty-one grams of isopropyl bromide and 40 grams of isopropyl iodide were added to 51 grams of carbethoxyhydroxamic acid dissolved in 25 cc. of absolute alcohol. The mixture was cooled and then an alcoholic solution of potassium hydroxide, containing a little less than the theoretical amount, was slowly added, with constant shaking of the mixture. The mixture was kept cool for a day, then allowed to stand at room temperature for three days, and finally heated to 90° for fifteen minutes to complete the reaction. The alcoholic solution was then treated in the usual manner, and 13 grams of α-isopropylcarbethoxyhydroxamic ester were obtained. The yield was 18.3 per cent. of the theoretical.

The next method which was tried was to isolate the sodium salt of hydroxyurethan and suspend it in alcohol. The theoretical quantity of isopropyl halide was added, and the mixture was then boiled under a reflux condenser for a day. The reaction mixture was then worked up, but a smaller yield of the ester was obtained than before.

The following method gave the best results: A mixture of 25 grams of hydroxyurethan, 29.3 grams of isopropyl bromide and about 15 grams of alcohol was boiled under a reflux condenser. An alcoholic solution of 13.3 grams of potassium hydroxide was added very slowly to the boiling solution. A heavy precipitate separated out. The resulting solution was then treated in the usual manner. Six grams of unchanged isopropyl bromide were recovered. Ten grams of α-monoisopropylcarbethoxyhydroxamic ester were obtained, representing a yield of 36 per cent.

α-Isopropylcarbethoxyhydroxamic ester,



, is a colorless oil boiling at 102°–103° under 12 mm. pressure. It is slightly soluble in water, and does not reduce ammoniacal silver nitrate solution. It colored ferric chloride purple, due to a trace of hydroxyurethan which was carried over with it. Unlike the other alkyl derivatives of carbethoxyhydroxamic acid, it has practically no odor.

0.3098 gram gave 0.5482 gram CO_2 and 0.2158 gram H_2O.

	Calc. for $C_6H_{13}O_3N$	Found
C	48.91	48.30
H	8.91	9.02

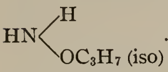
The ether solution containing the α,β-diisopropylcarbethoxyhydroxamic ester, which was left after the mixture of the mono- and diisopropyl esters had been extracted with potassium hydroxide solution, was dried and fractionated. An oil boiling at 101°–101°.5 under 15 mm. pressure was obtained. Eight and a half per cent. of the carbethoxyhydroxamic acid had been converted into the dialkyl derivative.

0.2760 gram gave 0.5754 gram CO_2 and 0.2524 gram H_2O.

	Calc. for $C_9H_{19}O_3N$	Found
C	57.09	56.85
H	10.13	11.76

α,β-Diisopropylcarbethoxyhydroxamic ester is slightly soluble in water. This solution gives no reaction with ferric chloride, ammoniacal silver nitrate or Fehling's solution. It has a pleasant odor, very much like that of phenylacetic ester.

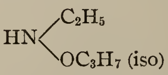
(*b*) *Preparation of α-Isopropylhydroxylamine,*

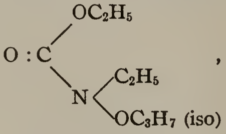

$HN\begin{cases} H \\ OC_3H_7 \text{ (iso)} \end{cases}$

.—The hydrolysis of the α-isopropylcarbethoxyhydroxamic ester was accomplished in the customary manner. Five and one-half grams of the ester, mixed with a solution containing 10 grams of potassium hydroxide, were heated at 100° for twenty-four hours. The free base was distilled from the aqueous solution and collected in dilute hydrochloric acid. This solution was concentrated and placed in a vacuum desiccator with potassium hydroxide and sulphuric acid. After two weeks α-isopropylhydroxylamine hydrochloride had crystallized out as white plates, melting at 84°.8, which were deliquescent. (Compare the isomeric *n*-propylhydroxylamine hydrochloride.) It is soluble in water and alcohol, but not soluble in ether. Its aqueous solution rapidly reduces silver nitrate and Fehling's solution in the cold.

Free α-isopropylhydroxylamine was obtained by distilling a mixture of 2 grams of the hydrochloride and 4 grams of dry potassium hydroxide. It is a colorless liquid boiling at 72°.2 (uncorr.). It has a disagreeable, pungent odor. Its specific gravity (25°/25°) is 0.8459. Its aqueous solution reduces ammoniacal silver nitrate solution and Fehling's solution.

VII. *α-Isopropyl-β-ethylhydroxylamine,*


$HN\begin{cases} C_2H_5 \\ OC_3H_7 \text{ (iso)} \end{cases}$

(*a*) *Action of Ethyl Iodide on α-Isopropylcarbethoxyhydroxamic Ester.*—A solution of 4.22 grams of sodium in absolute alcohol was slowly added to an alcoholic solution containing 27 grams of α-isopropylcarbethoxyhydroxamic ester and 28.6 grams of ethyl iodide. No noticeable change occurred. The mixture was allowed to stand for two weeks at room temperature, and was then heated to 70° for several hours. The small amount of fine precipitate was removed, most of the alcohol was distilled off, and after diluting the solution with water it was extracted with ether. The ether extract was shaken with dilute potassium hydroxide solution, and then shaken repeatedly with sodium thiosulphate solution to remove the free iodine which was present. It was then dried and fractionated under 748 mm. pressure. Twenty grams of α-isopropyl-β-ethylcarbethoxyhydroxamic ester,  $O:C\begin{cases} OC_2H_5 \\ N\begin{cases} C_2H_5 \\ OC_3H_7 \text{ (iso)} \end{cases} \end{cases}$, boiling at 181°–182° were obtained. The yield was 62.5 per cent. of the theoretical.

0.3499 gram gave 26 cc. N at 20° and 743.5 mm. pressure.

	Calc. for $C_8H_{17}O_3N$	Found
N	8.00	8.29

α-Isopropyl-β-ethylcarbethoxyhydroxamic ester is soluble in water, alcohol and ether. It gives no reaction with either ammoniacal silver nitrate, Fehling's solution or ferric chloride. It has a biting odor resembling phosgene.

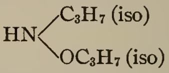
(*b*) *Preparation of α-Isopropyl-β-ethylhydroxylamine.*—Ten grams of the ester were treated in the usual manner with 20 grams of potassium hydroxide dissolved in water. The hydrochloride of α-isopropyl-β-ethylhydroxylamine, which was formed, remained as an oil upon evaporating the aqueous solution and drying in a desiccator over sulphuric acid. The aqueous solution of the salt reduced ammoniacal silver nitrate in the cold. Platinic chloride precipitated the chloroplatinate as a light yellow crystalline powder from an alcoholic solution of the hydrochloride.

0.1328 gram gave 0.0436 gram Pt.

	Calc. for $C_{10}H_{28}O_2N_2PtCl_6$	Found
Pt	32.19	32.83

When the hydrochloride is distilled with potassium hydroxide it gives α-isopropyl-β-ethylhydroxylamine. This is a colorless liquid boiling at 82°. It has an ammoniacal odor, and is not very soluble in water. Its aqueous solution reduces ammoniacal silver nitrate in the cold and Fehling's solution when heated. Its specific gravity (25°/25°) is 0.8730.

VIII. α-Diisopropylhydroxylamine,



$$HN\begin{cases} C_3H_7\ (\text{iso}) \\ OC_3H_7\ (\text{iso}) \end{cases}$$

A mixture of 13 grams of α,β-diisopropylcarbethoxyhydroxamic ester and 25 grams of potassium hydroxide dissolved in water were heated at 120° in a sealed tube for 36 hours. The contents of the tube were then distilled, and treated as usual. The hydrochloride of diisopropylhydroxylamine slowly crystallized out, mixed with ammonium chloride. The salt was recrystallized from alcohol. It formed flat plates, which melted at 74°.8.

Ten grams of powdered potassium hydroxide were poured over 5 grams of the hydrochloride contained in a distilling flask, and the mixture was warmed. Three and one-tenth grams of the free base were obtained. The yield was 82 per cent. of the theoretical. α-Diisopropylhydroxylamine is a colorless liquid boiling at 76.°6–77°. It has an ammoniacal odor mixed with that of an isocyanide. It is readily soluble in water, and rapidly reduces ammoniacal silver nitrate in the cold. It does not reduce Fehling's solution. Its specific gravity (25°/25°) is 0.8525.

The following table summarizes the properties of these compounds:

	Esters of hydroxyurethan	Alkylhydroxylamines		
		Free base		Hydrochloride.
	B. p.	B. p.	Sp. gr.	M. p.
α-Ethyl	195°–196° 95°–97° at 17 mm.	68° (Lossen)	0.8827 (Lossen) 7°.5	128° E. (Lossen)
α-Propyl	200°–210° E. 109°–111° at 15 mm.	86°.6–87°	0.8687	140°–141°
α-Isopropyl	102°–103° at 12 mm.	72°.2	0.8459	84°.8
α,β-Diethyl	72°–74° at 12 mm.	83° (Lossen)	0.829 at 0° (Lossen)	123°–124° (Jones)
α,β-Dipropyl	107°.5–108° at 20 mm.	85°–86°	0.8141	146°.6
α,β-Diisopropyl	101°–101°.5 at 15 mm.	76°.6–77°	0.8525	74°.8
α-Ethyl-β-propyl	189°	83°.8–84°	0.8033	72°.5–73
α-Ethyl-β-isopropyl	182° 84°–87° at 15 mm.	78°	0.8132	oil
α-Propyl-β-ethyl	92°.5 at 20 mm. 191°			96°.2
α-Isopropyl-β-ethyl	181°–182°	82°	0.8730	oil

SUMMARY

1. In the present paper methods of preparing the ethyl, propyl and isopropyl esters and mixed ethyl propyl and ethyl isopropyl esters of carbethoxyhydroxamic acid are described and the compounds studied. These esters are all high boiling oils with a characteristic odor. None of them reduce ammoniacal silver nitrate or Fehling's solution.

2. α-Propylhydroxylamine, α-isopropylhydroxylamine, and the different possible α-dialkylhydroxylamines containing ethyl, propyl and isopropyl groups, also their hydrochlorides and chloroplatinates, have been made and studied.

3. It has been shown that the esters of carbethoxyhydroxamic acid suffer hydrolysis with potassium hydroxide, the more easily the higher the molecular weight of the substituting group.[1]

4. The specific gravity of the dialkyl derivatives of hydroxylamine is less than the specific gravity of the monoalkyl derivatives of hydroxylamine, and all are specifically lighter than water. All boil between 70° and 90°.

5. The monoalkylhydroxylamines and the dialkylhydroxylamines containing two like groups are soluble in water, while the mixed dialkylhydroxylamines require a large amount of water for solution.

6. The aqueous solutions of the α-monoalkylhydroxylamines are energetic reducing agents. A second alkyl group in the molecule diminishes the reducing action.

In conclusion, I desire to express my sincere thanks to Dr. Lauder W. Jones, under whose direction the present work was carried out, for his kindly interest and many helpful suggestions and criticisms.

UNIVERSITY OF CINCINNATI
June 1, 1913

OBITUARY

JULIUS LEWKOWITSCH

Julius Lewkowitsch, who died at Chamonix, Switzerland, September 15th, after a brief illness, was born at Ostrowo,

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[1] Experiments made in this laboratory by Miss Leonora Neuffer on the secondary butyl derivatives confirm this statement.

Prussian Silesia, in 1857. Receiving his preparatory education in his native place, he went to Breslau, where he worked under Victor von Richter and won his Ph.D. degree in 1879 and that of M.A. in 1881. He then accepted a position at the Friedrichs Real Gymnasium, Berlin, under Landolt, and later became assistant to Victor Meyer at Heidelberg. During these years, he published a number of papers dealing with the action of nitric acid on fats and with stereochemical subjects, mandelic acid, optically active glyceric acids and leucine. He now turned to industrial chemistry and for a time was connected with tar and petroleum works. Going to England, he entered the employ of the Whitehall Soap Works at Leeds, and the remainder of his life was devoted chiefly to the technology of vegetable and animal oils and fats, a subject in which he became one of the world's greatest authorities. It was at Leeds that he, for the first time, succeeded in obtaining pure glycerol from soapmakers' lyes. Many of the processes now used in the utilization and analysis of these substances were devised or improved by him. In 1895, he started practice at Manchester as a Consulting Chemist and Technologist in Oils and Fats. Three years later he removed to London, and for many years acted as examiner for the City and Guilds of London Institute.

Lewkowitsch was a prolific writer and his works have come to be regarded as standards on their subjects. In 1895 he published his book on Oils and Fats, known in later editions as "The Chemical Technology of Oils, Fats and Waxes," the first volume of the fifth edition of which came from the press a few days before his death. French and German translations of this masterly work have also appeared. He also contributed the article on Oils and Fats to the Enclycopedia Britannica and the articles on these subjects and on Margarin to Thorpe's Dictionary of Chemistry and covered these fields in Meyer's "Jahrbuch der Chemie" and Lunge's "Chemisch-technische Untersuchungsmethoden." Among his other books may be mentioned his "Laboratory Companion to Fats and Oils Industries," which has also been translated into German. His total contributions to scientific literature number about 140.

He early became connected with the "Journal of the Society of Chemical Industry," first as Abstractor, then as a member of the Publication Committee, and served on the Council and as Vice-President of the Society. He was Chairman of the London Section at the time of the meeting of the International Congress of Applied Chemistry at London, and his remarkable linguistic versatility is shown by the fact that he addressed that gathering in English, German, French and Italian. In 1911, he was made Foreign Secretary of the Society, a position he held at the time of his death. He also served on the Councils of the Institute of Chemistry, of the London Chemical Society and of the Society of Public Analysts. In 1909 he was awarded the Lavoisier medal of the French Chemical Society.

REVIEWS

A TEXTBOOK OF CHEMISTRY. By WILLIAM A. NOYES, Director of the Chemical Laboratory of the University of Illinois. New York: Henry Holt and Company. 1913. pp. xv + 602.

The author tells us that: "This book is the result of twenty-five years of experience in teaching chemistry to classes of students, some of whom were beginning the subject while others have had an elementary course in the High School. It is intended to make the presentation sufficiently complete and clear so that college students who have had an elementary course in physics may use the book successfully, without any previous study of chemistry. At the same time it is believed that the book is of such a character that the college students who use it after taking a course in the High School will not feel that they are wasting their time."

The book is clearly written and is, no doubt, accurate. What especially distinguishes it from most other books prepared for the same general purpose is the amount of space devoted to the newer theories. Descriptive chemistry is, however, not treated as if of minor importance.

Opinions differ as to how profitable it is for college students beginning the subject to attempt to acquaint themselves with all the latest conceptions, some of which it is impossible for them even faintly to comprehend. Assuming that it is well for them to make the effort, this book can be highly recommended as a guide.

The author is unusually cautious and this has led him to use such expressions as "for some reason," p. 8; "it is well, however, to recognize how imperfect and fragmentary our knowledge is and that there are hundreds of questions like these for which we have no answer," p. 28; "This is another of those questions, like the cause of heat generated when elements combine, which waits for an answer," p. 29; "for other reasons which we do not fully understand," p. 50; "Other factors are involved, and some of these are, at present, but little understood," p. 52; "No satisfactory reason for such differences has been discovered," p. 79; "but we can form only a very vague idea of the mechanism of the action," p. 105; "The reason for this catalytic effect of the water is not understood," p. 105; "but it is also connected with the change in volume which occurs in the reaction and with other factors which are less clearly understood," p. 110; etc.

Such expressions show, to be sure, that the state of mind of the author is thoroughly scientific, but it is fair to ask whether they are wise pedagogically? A certain amount of dogmatism is necessary in teaching beginners, otherwise there is some danger that they will take all statements with a grain of salt. The writer recalls an experience of his early years, when he was beginning his work as a teacher. He was at that time, and is still, very much impressed by the immensity of the unknown and in lecturing he was apt to use the expression "but, in fact, we know very little about this subject." One day, on pressing a student who had struck bottom in recitation, he was amused and surprised and made wiser by the answer: "We know very little about this subject, professor." The professor was extremely cautious after that in using that expression. This is not intended as a suggestion that Professor Noyes's book is seriously marred by the tendency illustrated. It isn't. In the opinion of the writer the book is an excellent one and deserves a conscientious trial. I. R.

OUTLINES OF THEORETICAL CHEMISTRY. By FREDERICK H. GETMAN, Ph.D. (Johns Hopkins), Associate Professor of Chemistry in Bryn Mawr College. New York: John Wiley and Sons, Inc. London: Chapman and Hall, Ltd. 1913. pp. 467. Price, $3.50.

The author of this admirable little book states in his preface that "the present book is designed to meet the requirements of classes beginning the study of theoretical or physical chemistry. A working knowledge of elementary chemistry and physics has been presupposed in the presentation of the subject, the introductory chapter being the only portion of the book in which space is devoted to a review of principles with which the student is assumed to be already fairly familiar. With the exception of a few paragraphs in which the application of the calculus is unavoidable, no use is made of the higher mathematics, so that the book should be intelligible to the student of very moderate mathematical attainments."

The "contents" and order of arrangement of the material are just about what one would expect in a book designed for elementary students in "general chemistry."

The most striking features of the book are: it is written in clear, and, usually, choice English, from which all of the life has not been taken by repeated revision. The illustrations are admirably drawn, and the publishers have done a good piece of "book-making." It is to be hoped that this book will find a demand that is commensurate with its pronounced merits. H. C. J.

ELEMENTARY CHEMISTRY, with Special Reference to the Chemistry of Medicinal Substances. By H. M. GORDIN, Professor of Chemistry in the Schools of Pharmacy and Dentistry of the Northwestern University. Vol. I, Inorganic Chemistry. Chicago: Medico-Dental Publishing Co. pp. 482. Price, $3.00.

The author's purpose in writing this book may best be understood by the following quotation from the preface: "The book is intended primarily for those studying for, or engaged in, the professions of pharmacy, medicine and dentistry. In addition to the material usually treated in elementary text-books on inorganic chemistry, it contains most of the inorganic chemicals, both official and non-official, employed as medical agents." The book is not intended for a laboratory manual, but as an explanation of the chemical principles "underlying the preparation, indentification, and assay of substances used in the healing professions." Several chapters on energy, matter, physical and chemical changes, gas laws, molecular and atomic hypotheses, the determination of chemical formulas, and chemical equations serve as an introduction. Theoretical chapters on valence, solution, electrolysis, ionic theory, etc., are then interspersed with the usual description of the elements and their compounds. However, one notes the lack of the application of these principles to specific examples. The treatment of the theoretical side is simpler than in most similar text-books, but in some cases accuracy is sacrificed to simplicity and reminds one of kindergarten methods. Thus on page 5 we read of substances being divided into "ponderable substances" and "imponderable substances," and a few lines below, "heat and electricity are examples of imponderable substances." On page 48, "ready-made hydrogen," on page 54, "ready-made oxygen," on page 113, "that substance which is made to disappear in the other is said to be dissolved," and on page 178, "to fence off the elements into closed groups," are rather unusual.

A medical atmosphere is given the book by brief descriptions of various pharmacopeial tests, but these are too incomplete to be of any use in the actual performance of the test. The various methods of balancing equations receive a very full discussion, and a set of questions and problems concludes each chapter. E. K. MARSHALL, JR.

COURS ÉLÉMENTAIRE DE CHIMIE ET DE MINÉRALOGIE. Par DR. C.-I. ISTRATI, Professeur de Chimie organique à l'Université de Bucarest, et DR. G.-G. LONGINESCU, Professeur de Chimie inorganique à l'Université de Bucarest. Avec une Préface de CHARLES FRIEDEL, Membre de l'Institut. Deuxieme édition française, publiée d'aprés la quatrième édition roumaine par A. ADAMS, Professeur agregé au Lycée de Charleville. Paris: Gauthiers-Villars. 1913. pp. xii + 402. Price: paper, Fr. 13.00; cloth, Fr. 14.50.

Owing to the space devoted to mineralogy and the attempt to cover the fields of both organic and inorganic chemistry, the explanations and statements are in many cases brief and unsatisfactory. J. E G.

LABORATORY EXPERIMENTS IN GENERAL CHEMISTRY. By H. B. NORTH, Ph.G., D.Sc., Associate Professor of Chemistry in Rutgers College. 36 illustrations. New York: D. Van Nostrand Co. 1913. pp. v + 205. Price, $1.00.

The experiments in this book, amounting to 500, have been so selected that from them a sufficient number can be chosen to accompany the use of any text-book and to suit any class of students. The experiments are well selected, well presented and especially emphasize the quantitative side of the reactions. The book is well printed and makes an excellent impression. Those who are conducting courses in general chemistry should examine the book carefully as it could be used to great advantage in place of some of the manuals which are now being employed. J. E. G.

QUANTITATIVE ANALYSIS BY ELECTROLYSIS. By ALEXANDER CLASSEN, with the Coöperation of H. CLOEREN. Translated from the Thoroughly Revised Fifth German Edition by WILLIAM T. HALL, Assistant Professor, Massachusetts Institute of Technology. New York: John Wiley & Sons, Inc. London: Chapman & Hall, Ltd. 1913. pp. xiv + 308. Price, $2.50.

The German original of this work is so well and favorably known that it is only necessary to note that the translation has been prepared by Prof. Hall to insure for it a welcome by all English-speaking chemists who ever have occasion to make electrolytical analyses. Prof. Hall has made but few changes. He has adopted the system of notation recommended in the report by the Committee on the Notation of Physicochemical Quantities which was submitted to the Council of the American Chemical Society in March, 1912. The typography, illustrations, paper and binding are up to the Wiley standard. C. A. R.

QUANTITATIVE ANALYSIS IN PRACTICE. An Introductory Course Designed for Colleges and Universities. By JOHN WADDELL, B.A. (Dalhousie University), B.Sc. (London), Ph.D. (Heidelberg), D.Sc. (Edinburgh), Assistant Professor of Chemistry, School of Mining (Queen's University), Kingston, Canada. London: J. & A. Churchill. Philadelphia: P. Blakiston's Son & Co. 1913. pp. vi + 162. Price, $1.25.

In the opinion of the reviewer the strong feature of this book is the completeness and discrimination with which the precautions necessary for exact results are described. In almost every case the student is told how to work in a most approved fashion. One serious omission is that the advisability of washing precipitates with a solution of precipitant is not always mentioned, although this procedure is recommended in some instances. The discussions of the various difficulties and remedies are on the the whole satisfactory, but it is a pity that the Electrolytic Dissociation Hypothesis is not applied in the main body of the text instead of being confined to an appendix. There the common ion effect on the solubility of precipitates is discussed and applied to the question of completeness of a precipitation, but not to the washing of precipitates. One might criticize also the omissions of any discussion of significant figures, of the determination of nitrogen in the chapter headed "Water Analysis" and of any directions for making sure that the solution is homogeneous before the final setting in adjusting the volume of a standard solution. For pedagogical purposes a table of atomic weights would be more useful than a table of factors. The style occasionally becomes colloquial but it is clear. For instance, the meaning of the direction, "squirt off the cover glass into the casserole," is unmistakable, even if the expression lacks finish. G. P. B.

QUALITATIVE ANALYSE VOM STANDPUNKTE DER IONENLEHRE. Von DR. WILHELM BÖTTGER, A. O. Professor und Oberassistent am phys.-chem. Institut der Universität Leipzig. Dritte Auflage. Mit 26 Figuren im Text, einer Spektraltafel und besonderen Tabellen zum Gebrauche im Laboratorium. Leipzig: Verlag von Wilhelm Engelmann. 1913. S. xvii + 565. Preis, geh., M. 11.20; geb., M. 12.50.

The appearance of the third edition of this very comprehensive treatise on the theory and practice of qualitative analysis is a sufficient indication of its popularity. It is unquestionably the very best modern book on the subject. The third edition, in matter and arrangement, is very similar to the second. Microchemical reactions constitute a new feature. Somewhat more attention is given to colloids and the chapter on oxidation and reduction has been largely rewritten. B. F. L.

QUALITATIVE CHEMICAL ANALYSIS. A Laboratory Guide. By WILFRED WELDAY SCOTT, A.M., First Assistant Chemist, General Chemical Company, Laurel Hill, N. Y. City, Instructor of Quantitative Analysis, Pratt Institute, Brooklyn. Illustrated. Second Edition, Thoroughly Revised. New York: D. Van Nostrand Co. 1913. pp. xi + 167. Price, $1.50.

The first edition of this book was very favorably reviewed by Prof. Renouf in THIS JOURNAL.[1] The present edition "has been thoroughly revised, portions rewritten and useful material added." The principal changes noted are the addition of a table of atomic weights, rapid qualitative tests for lead, antimony, tin and copper in alloys, Hinds's method for the precipitation of the hydrogen sulphide group and the separation of its divisions, Allen and Palmer's modified Gutzeit method for arsenic, and tests for salicylic acid.

C. A. R.

PRACTICAL CHEMISTRY. Qualitative Exercises and Analytical Tables for Students. By the late J. CAMPBELL BROWN, D.Sc., LL.D., Professor of Chemistry in the University of Liverpool. Sixth Edition, edited by GUY D. BENGOUGH, M.A., D.Sc. London: J. & A. Churchill. 1913. pp. 78. Price, 2s. 6d.

The author has adopted the usual methods of separation and treatment of the subject, but he has added a section on the reactions of the rare metals and has omitted reference to the relations of the modern theories of ionic reactions and of the mass law to qualitative analysis. J. E. G.

DIE APPARATFÄRBEREI DER BAUMWOLLE UND WOLLE unter Berücksichtigung der Wasserreinigung und der Apparatbleiche der Baumwolle. Von E. J. HEUSER. Mit 191 in den Text gedruckten Figuren. Berlin: Verlag von Julius Springer. 1913. pp. v + 301. Price, M. 8.00.

To one accustomed to the English books on dyeing and bleaching apparatus, this book immediately impresses the reader as being something different. Although containing nearly two hundred illustrations, there are none of the stereotyped ones which have appeared with great regularity in nearly every English book on the subject since the time of Hummel. It is, strictly speaking, a German book, for only one English and no American machines are described.

The book is divided into four parts: Part I (44 pages) is devoted to a description of apparatus for the purification of water for textile purposes. The recently introduced Permutit system of purification, which has attracted so much attention, is taken up with considerable detail. Part II is divided into two sections, the first (40 pages) being devoted to machinery for bleaching cotton material. All manufacturers of cotton cloth woven from dyed yarn realize the great advantages to be derived from a successful cop-dyeing process. Much time and money have been spent in experimenting along this line, particularly in Germany, and those interested in this type of apparatus will find the descriptions and discussions in this book very complete. Part III (65 pages) is devoted to the dyeing of wool in the loose state, and at the different stages of its manufacture into cloth. The modern tendency in dyeing wool as well as cotton is towards the circulatory process, *i. e.*, a process in which the material is kept stationary while the dyeing liquor is circulated through it. Worsted top dyeing by this general method has been in use for a number of years, and the tendency is more and more toward the dyeing of loose wool and even yarn by this method. The Germans have progressed quite rapidly in this direction, and a number of machines of this type are fully described. Part IV (23 pages) is devoted to drying and hydro-extracting apparatus. The book closes with an excellent index which gives, in a tabulated form, the manufacturer's name, use of, number of the illustration, and pages of description for each machine mentioned in the text.

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[1] Vol. 46, p. 314.

This book will prove a valuable addition to any textile library and should be carefully examined by every progressive colorist. To those interested in textile coloring, though unfamiliar with the German language, a perusal of this book will prove of value, on account of the numerous and excellent illustrations which it contains.

L. A. OLNEY

UNTERSUCHUNG UND NACHWEIS ORGANISCHER FARBSTOFFE AUF SPECTROCHEMISCHEM WEGE. Von JAROSLAV FORMÁNEK, o. Professor an der k. k. Böhmischen Technischen Hochschule in Prag, unter Mitwirkung von DR. EUGEN GRANDMOUGIN, Professor an der Höheren Chemieschule in Mülhausen i/E. Berlin: Verlag von Julius Springer. Zweiter Teil. 1 Lieferung, 1911. S. 164 mit 6 lithographischen Tafeln. Preis, M. 10.00. 2 Lieferung, 1913. S. 165–366 mit 7 lithographischen Tafeln. Preis, M. 14.00.

The first 56 pages are devoted to the classification of organic dyestuffs. The remainder of the two parts of the book (310 pages) gives a description of the absorption spectra of a large number of dyestuffs in various solvents, following the accepted system of classification. The plates give a schematic and qualitative illustration of the data given in the tables. They are very useful in giving a picture of the system of classification.

Dyestuffs are divided into four main "natural" groups: the green (blue-green), the blue (green-blue, blue-violet and violet), the red (violet-red, yellow-red) and the yellow (orange-yellow and brown) dyestuffs. The main groups are again subdivided. The tables of data include only the green, blue and red dyestuffs. At the end of each table is given a list of the dyestuffs arranged alphabetically. About 400 green, 1100 blue and 900 red compounds are described.

The problem of determining the kind of compound in a dyestuff is treated in detail throughout the following processes: the preparation of a solution of the dyestuff; the determination of the wave length of the absorption bands; the development of characteristic reactions; and the use of the author's tables. A section is devoted to mixtures of dyestuffs.

This treatise is well written and presents a well-classified mass of data on the absorption spectra of colored organic compounds. It should prove of inestimable value to chemists whose problems include the detection of the nature of organic coloring matter. Spectroscopy is greatly indebted to the extensive and careful work of J. Formánek. W. W. STRONG

THE PRINCIPLES OF APPLIED ELECTROCHEMISTRY. By A. J. ALLMAND, D.Sc. Illustrated. New York: Longmans, Green & Co. London: Edward Arnold. 1912. pp. x + 547. Price, $5.00.

Part One of this treatise consists mainly of a very satisfactory, if brief, outline of the theory of solutions, with special reference to the applications to various electrochemical processes. It is this feature which distinguishes the present text from most works in English on applied electrochemistry. The early chapters deal with equilibrium reactions, Faraday's laws, osmotic pressure, conductivity and dissociation, energy relations, electrolysis and polarization, cathodic and anodic processes, etc. These topics are necessarily discussed briefly, the author assuming on the part of the reader a knowledge of the fundamentals of chemistry and electricity. In thus emphasizing the theoretical side of the subject the present work marks a distinct advance over the usual practice in writing texts in English.

Part Two gives a description of the various technical processes of importance, including processes for the manufacture of numerous chemicals, such as hypochlorite, chlorates, alkali, permanganate, carborundum, carbon bisulphide, etc., and various electrometallurgical processes. Throughout this part the close relation between theory and practice is pointed out.

The book is distinctly pleasing and shows plainly that the author has spared no efforts to make it as free as possible from those imperfections which usually mark first editions. The chief regret which the reader feels is that metallurgical processes have not received more extended treatments, but this, of course, could not have been done without materially increasing the size of the volume, already large. B. F. LOVELACE

DIE OXYDATION DES AMMONIAKS ZU SALPETERSÄURE UND SALPETRIGERSÄURE. Von PROF. ED. DONATH und ING.-CHEMIKER A. INDRA in Brünn. Mit 10 Abbildungen. Sammlung chemischer und chemisch-technischer Vorträge. Begründet von F. B. Ahrens: herausgegeben von Prof. W. Herz, Breslau. XIX Band, 4/6 Heft. Stuttgart: Verlag von Ferdinand Enke. 1913. pp. 108.

In this monograph the authors have given a fairly complete and satisfactory résumé of the literature relating to the sources of ammonia and the methods used commercially for the oxidation of ammonia to nitrous and nitric acids. B. F. L.

CHEMICAL GERMAN. An Introduction to the Study of German Chemical Literature, including Rules of Nomenclature, Exercises for Practice and a Collection of Extracts from the Writings of German Chemists and Other Scientists and a Vocabulary of German Chemical Terms and Others Used in Technical Literature. By FRANCIS C. PHILLIPS, Professor of Chemistry in the University of Pittsburgh. Easton, Pa.: The Chemical Publishing Co. 1913. London: Williams & Norgate. pp. xi + 241. Price, $2.00.

The present book "contains rules of nomenclature interspersed with exercises intended to illustrate the use of German chemical terms pertaining to general chemistry, inorganic and organic, and to the various processes of the laboratory. These are followed by a collection of extracts from the writings of noted German chemists, having in many cases direct bearing upon the history of chemistry. A vocabulary of the more common German terms used in chemistry will aid the student in his translations. The work is intended for students who have had at least a year of German and who have mastered the elements of chemistry." A list of abbreviations frequently found in German chemical literature is also given.

A student who has conscientiously worked his way through this book should find no difficulty in reading any German article bearing on chemistry. He will find himself also in possession of a most interesting collection of extracts which alone make the book well worth owning. C. A. R.

THE 'WELLCOME' PHOTOGRAPHIC EXPOSURE RECORD AND DIARY. 1914. U. S. A. Edition. New York: Burroughs Wellcome and Co. pp. 280. Price, 50 cents.

Every owner of a camera should possess a copy of this beautifully gotten up and useful little book.

"It condenses into one small volume clear, definite and precise instructions on a very wide range of subjects. All the little wrinkles and dodges which long experience has taught the successful worker are here analyzed and set forth in simple formulas and exact directions such as help the beginner and serve as a useful reminder to the expert. Development, toning, fixing, printing, the various processes of production in warm tones and colors, and the methods of dealing with errors of technique are explained, particular attention being directed in the 1914 edition to the green and blue toning, and the production of various colors by development and other methods. On the subject of exposure this book is the last word, containing, in addition to its light tables for each month and factors for plates and films, the special device attached to the cover which tells the correct exposure at one turn of the disc." It is provided with blank ruled pages to record negative and positive exposures and for daily memoranda, and is substantially and tastefully bound in red cloth. It should prove a "Wellcome" gift to any camera enthusiast.

C. A. R.

A NEW ERA IN CHEMISTRY. Some of the More Important Developments in General Chemistry during the Last Quarter of a Century. By HARRY C. JONES. New York: D. Van Nostrand Company. 1913. pp. xii + 326. Price, $2.00.

Any book from the pen of Professor Jones is welcome, and no book more acceptable than a review of modern chemistry from his standpoint, regarding which he could write as few others, "quorum pars fui." Then his own enthusiasm for his subject is so great that it cannot fail to be contagious, and even abstruse topics in physical chemistry become as entertaining as romance; indeed in the author's hands much of the history of modern chemistry is a real romance, romance of fact more entrancing than any romance of fiction.

The purpose of the book is laid down in the preface: "It is, however, clearly recognized that there is a difference between the chemistry of twenty-five years ago and that of today. That this is really a difference in kind is not always clearly understood by those who have watched the development during that period, or by those who have not studied chemistry long enough to have the necessary perspective. It has seemed desirable to point out as clearly as possible in what this difference consists; how these new developments were brought about and by whom. This is the object of this little work. My apology for adding another book to the literature of chemistry is that I have lived during the 'New Era,' have known well most of the men who have been instrumental in bringing it about, and have been a student of the three leaders in this movement—Van't Hoff, Arrhenius and Ostwald." And it is this personal element which lends such a charm to the book.

The first chapter is entitled "Condition of Chemistry in

1887," and is a brief résumé of chemical history up to that time, with the emphasis well put on the salient points. The author's viewpoint is made clear by his characterization of the period up to 1887 as the "fact discovering" or "brick making" period, "very important in itself and absolutely essential to the subsequent development of a science of chemistry." "It was, however, not a science of chemistry," but a system. The year 1887 marks roughly "the beginning of the transition from a system into a science of chemistry." Of course, there are those who might differ from this opinion and incline to the view that there was at least the beginning of a chemical science at an earlier period; indeed, some of us thought that we were engaged in studying science as we listened to the lectures of Wöhler and Hofmann and worked in the laboratory under Hübner and Tiemann and Liebreich, and surely we were just as happy over it as if we had been doing *real* scientific work under Ostwald and Nernst; I must admit, though, that there would have been more real enthusiastic inspiration under the genial author of this book, and in view of this enthusiasm we can pardon his strong partiality for modern chemical *science*.

The next chapters trace the development of the law of mass action, up to the work of Guldberg and Waage; the thermochemical work of Thomsen, Hess and Berthelot; the development of stereochemistry by van't Hoff, Pasteur, LeBel and Guye; the phase rule of Willard Gibbs. And here we must pause to quote the last paragraph of this chapter: "Looking at the Phase Rule in as broad and impartial a manner as possible, I am unable to get away from the thought that by certain men it has been an overridden hobby." We wonder if there are not other phases of modern chemical science which might be classed as overridden hobbies; and yet in their masters' eyes they are beautiful steeds.

I doubt if the subjects of osmotic pressure and electrolytic dissociation have ever been as completely, succinctly and withal attractively treated as in the 60 pages of this book devoted to them. The vividness of description may be judged by the following: "I have seen the following experiment performed. Pure, dry sulphuric acid in a tube, and a piece of very carefully dried metallic sodium plunged into it. The sodium remained suspended in the acid just as quiescently as it would in ligroin." Surely pages of statement would less effectively illustrate the rôle of water.

Not least in interest or in importance is the chapter on the solvate theory of solution, for here we have Jones's own work set forth with conclusive logic. It has been his task to apply the theories of ideal solutions to the actual solutions one meets in the laboratory and in every-day life, and hence he has given us "a theory of solutions in the broad sense of that term."

To the work of Ostwald and his students and co-workers (shall we be considered purists if we object to the unhyphenated "coworkers"?) are devoted the two longest chapters of the book. We are forced to agree with our author in his enthusiastic admiration of his great, many-sided teacher. If Ostwald did not create modern chemical science, he at least compelled the universal recognition of the fact that it is a science, however narrowly one may define the word. In this connection is treated the work of Beckmann, of Nernst, of LeBlanc, of Bredig, of A. A. Noyes, of Richards, and of others who have been leaders of the modern era.

The last chapter is devoted to the Electron and Radiochemistry, an excellent recapitulation of the development of this field, brought down to the present day. The book concludes with an appendix containing charming personal impressions and reminiscences of Mendeléeff, Kekulé, Gibbs, Ramsay, van't Hoff, Arrhenius, and, above all, Ostwald. May we again quote: "A visit of a day to Ostwald at Gross-Bothen is worth a trans-Atlantic trip. You cannot be in his presence for ten minutes without realizing that you are facing a really great man. His breadth of knowledge, his depth of interest, his unbiased judgment of men and ideas, his originality and many-sidedness, all taken together, make him one of the most interesting personalities of the age. * * * * * He has lived to see chemistry largely transformed from empiricism and system into science, due in no small measure to his own organizing power. An original and systematic mind, a kindly and generous heart, a many-sided genius is Wilhelm Ostwald."

Verbum sat. No chemist, be he teacher, student or technologist, should fail to read this book, whether to learn for the first time what modern chemistry is doing, or to review systematically what he already knows but in disjointed sections, or merely to while away a few leisure hours in reminiscing over his own work. As a whole, the book comes pretty near being a philosophy of modern chemistry. JAS. LEWIS HOWE

THE SYNTHETIC DYESTUFFS AND THE INTERMEDIATE PRODUCTS FROM WHICH THEY ARE DERIVED. By JOHN CANNELL CAIN, D.Sc. (Manchester and Tübingen), Editor of the *Journal of the Chemical Society*, Examiner in Coal Tar Coloring Matters to the City and Guilds of London Institute, and JOCELYN FIELD THORPE, D.Sc. (Manchester), PH.D. (Heidelberg), F.R.S., F.I.C., Sorby Research Fellow of the Royal Society, Late Lecturer on Coloring Matters in the University of Manchester. Second Edition, Revised. London: Charles Griffin & Company, Limited. 1913. pp. xvii + 1423. Price, 16s.

This book is a most excellent treatise on this difficult and complicated chapter of organic chemistry. It is divided into the following four parts: Theoretical, Practical, Analytical, and Appendix, containing tables of specific gravities of solutions, etc. The theoretical part contains a discussion of coal tar, and the various classes of intermediate products, and 16 chapters devoted to the dyes themselves. The practical part gives a description of the technical laboratory and the preparation of the intermediate products and the dyestuffs themselves. The analytical part gives the analytical methods, the behavior of the principal fibers toward dyes, and the reactions of the dyes on the fiber. The text is clear and the use of graphical formulas is a great aid in the presentation of the subject.

S. F. A.

COURS DE CHIMIE ORGANIQUE. Par FRÉD. SWARTS, Professeur à l'Université de Gand, Membre de l'Académie Royale de Belgique. 2^e édition revue et augmentée. Avec figures. Paris: A. Hermann & Fils; Gand: Ad. Haste. 1913. pp. vi + 754. Price, Fr. 15.00.

The second edition of this book is a general treatise on organic chemistry, suitable for college students. The arrangement is good, the text is clear, and the use of graphical formulas is commendable.

S. F. A.

RECENT ADVANCES IN ORGANIC CHEMISTRY. By A. W. STEWART, D.Sc., Lecturer on Organic Chemistry in the Queen's University, Belfast. With an Introduction by J. NORMAN COLLIE, PH.D., LL.D., F.R.S., Professor of Organic Chemistry in University College, London. Second Edition. London, New York, Bombay and Calcutta: Longmans, Green & Co. 1911. pp. xv + 320. Price, $2.50, net.

The second edition of this well-known and excellent treatise still imbues the reader with the spirit of the rapid progress made to-day in the theories of organic chemistry. The chapters on the Grignard reaction and the chemical action of light have been replaced by a chapter on quinoles and another on the triphenylmethyl problem. The book deals with such important chapters as the polymethylenes, the terpenes, the alkaloids, the purines, the polypeptides, the polyketides, the quinoles and the triphenylmethyl question, each of which is treated in a thorough way.

S. F. A.

TABELLE DER WICHTIGSTEN ORGANISCHEN VERBINDUNGEN, geordnet nach Schmelzpunkten. Zuzammengestellt von DR. RICHARD KEMPF, Assitent am Königl. Materialprüfungsamt zu Berlin-Lichterfelde. Braunschweig: Druck und Verlag von Friedr. Vieweg & Sohn. 1913. pp. xi + 135. Price, M. 8.80.

The title shows the object of this author in writing, or, rather compiling, this little book. About 2500 of the most common compounds are characterized in this volume by the melting point, color, boiling point, name, graphical formula, and by the citation to the original literature and to Beilstein. Although its range is too limited, it should prove very useful as a handbook. S. F. A.

METALLURGICAL ANALYSIS. By NATHANIEL WRIGHT LORD, Late Professor of Metallurgy and Mineralogy, Ohio State University, and DANA J. DEMOREST, Professor of Metallurgy, Ohio State University. Third Edition. International Chemical Series, H. P. TALBOT, PH.D., Consulting Editor. New York: McGraw-Hill Book Co., Inc. 1913. pp. xvii + 334. Price, $2.50.

This book was originally issued in 1893 as a small volume of of 100 pages, the second and enlarged edition being published ten years later, and now comes this third edition "re-written so as to incorporate in the old methods the recent advances in knowledge bearing on them." "Also many new subjects have been added so as to include in the book practically all the methods likely to be used by the metallurgical chemist."

The book was originally intended for the use of the late Professor Lord's students, but in its second and third editions it has grown away from the student or teaching point of view and the more technical side has been developed. In this development the book has undoubtedly suffered from growing pains and it consequently appears very uneven in character. Evidently the attempt has been made to include everything necessary for the worker in the metallurgical field, without reference to previous training, and little is left to the imagination. Original imperfections have been transmitted, and many others added, in this edition. The English in places is distinctly of the busy, commercial laboratory type where results are of first importance and manner of presentation an unimportant detail. There is, in places, an uncertainty of statement which would be particularly annoying to the earnest student, such as "water *is said* to decompose the precipitate to a slight extent," "the phosphoric acid *is also said* to prevent the reduction of the permanganate by HCl," "*probably* contains a complex compound," "*perhaps* as $Fe_xCl_y(OH)_z$," "changes *principally* to Mn_3O_4." The untrained will not care about the real truth, but others will want to know.

Some preliminary knowledge of quantitative analysis is assumed, but if the worker is weak on calculations he may get his results by following directions and making a proportion but he will have learned little about principles involved. Instead of insisting on always weighing "factor weights" and multiplying by some decimal number to get percentages, it would have been much preferable to have explained the principles once for all. There is, to be sure, a chapter of two pages at the end of the book on "Calculation of Normal Solutions," which is, if the subject is to be treated at all, badly placed and inadequate. In some places the weighed precipitate is said to contain a certain percentage of the element desired, and again such statements as this, referring to $Mg_2P_2O_7$, "this contains 0.279 of phosphorus." There is much unevenness of this character in dealing with calculations.

In each chapter there is a description of the method employed, and this is preceded in all cases by a statement of principles and in most cases by a series of notes bearing upon the methods. A much more logical treatment of the subject would have been to have given the procedure first and then have the notes follow the method. This is particularly objectionable from a teacher's point of view, as the discussion of the method is given before the student knows anything of the process employed.

The book is essentially a collection of methods in ferrous and non-ferrous metallurgy covering a wide field and containing much excellent material but very poorly digested and not very logically treated. H. F.

LIQUID AIR, OXYGEN, NITROGEN. By GEORGES CLAUDE, Engineer Laureate of the Institute of France. English Edition, Corrected and Brought up to Date by the Author. Translated by HENRY E. P. COTTRELL, Assoc. M.I.C.E., M.S.C.I., F.R.C.I. With a Preface by D'ARSONVAL, Member of the Institute of France. Philadelphia: P. Blakiston's Son & Co. 1913. pp. xxv + 418. Price, $5.50.

This book is a treatise on the liquefaction of gases, with special reference to the author's own application of theory to the production of liquid air, oxygen and nitrogen, the latter by partial condensation. While other processes are given, the successful development of Claude's method of expansion with external work is most fully and graphically described.

The book is divided into four parts: Part I, on Liquefaction of Gases, is a historical résumé of the subject, down to the liquefaction of helium. Part II, on The Commercial Liquefaction of Air, is largely a theoretical discussion and comparison of the two methods of expansion, with or without external work. Part III is on the Preservation and Properties of Liquid Air, and may well be in the original a verbatim report of the author's lectures, in such popular and entertaining style is it written. Part IV, on The Separation of the Air into Its Elements, is the most original portion of the book, and describes and discusses the various methods, theoretical and in practical use, for the commercial production of oxygen and nitrogen from the air. The last chapter enumerates, with illustrations, the principal plants having Linde installations as well as those of Claude.

More than 150 illustrations are used in the book, which is most attractively gotten up, and is valuable for reading as well as for reference. The translation is calculated to mar one's enjoyment of the book, so poorly is it done. J. L. H.

Über Natronzellstoff, seine Herstellung und chemischen Eigenschaften. Von Dr. Ing. Christian Christiansen, Diplomingenieur. Schriften des Vereins der Zellstoff- und Papier-Chemiker. Heft 6. Berlin: Verlag von Gebrüder Borntraeger. 1913. pp. 154. Price, M. 5.00.

This monograph on the soda cellulose process consists of 133 pages of subject matter and an appendix of 11 pages which gives a chronological list of references to the patent and general literature.

The first 59 pages take up a historical review of the various alkaline processes, the composition and utilization of the waste liquors, recent technical accomplishments, the recovery of alkali, the control of manufacturing conditions and the theory of cooking. This portion of the work is fairly well covered though the author does not quote from actual manufacturing results as much as would seem desirable and also distinctly avoids an expression of personal opinion. On the whole, it may be said of this part of the work that it contains little which will be new to the man who is well up in the chemistry of the process though it may be of material assistance to the rule-of-thumb man.

The remainder of the monograph is given over to experimental work and a discussion of its results, starting with an outline of the work and continuing with a discussion of the course of the soda process, the relation between alkali consumption, yield, properties of the cellulose, etc., and suggesting technical applications and methods of controlling the cooking process. Tables are given showing the cooking results as well as the chemical constants of the various pulps, as copper number, hydrolysis number, resin and wood gum determinations, etc. Curves for a number of cooks are also given which show the relations of a number of the important factors and lay particular stress on the periods during which the consumption of caustic soda ceases. Finally there are detailed descriptions of 24 cooks made in a jacketed digester by the straight soda process, and details of the methods employed in testing the fiber produced.

The experimental work involved was large in amount and appears to have been carried out with great care, yet certain facts render the results of less value than they should be. No statement is made of the kind of wood used, the conclusions are drawn from very small differences in yield and appearance and the location and duration of the constant points depend on the analyses of samples of 1 cc. of black liquor by a titration method which is not of the highest accuracy. The method of calculating the proportion of alkali is also given, yet when one recalculates the figures given in the detailed cooks 16 out of 24 are not found to correspond to the numbers published. In the case of Cook 1 the yield given on p. 96 is 67 per cent. while in the table on p. 64 it is given as 75 per cent.

In spite of these criticisms the reviewer considers this work to be valuable because of the way in which the subject has been approached and because it is suggestive of an immense amount of work which it seems desirable to perform. The book can be read to advantage by all who are interested in the scientific control of the soda process but will prove of somewhat less interest to those working by the sulphate process.

E. SUTERMEISTER

AN INTRODUCTION TO THE CHEMISTRY OF PLANT PRODUCTS. By PAUL HAAS, D.Sc., PH.D., Lecturer on Chemistry, Royal Gardens, Kew, Demonstrator of Chemistry and Toxicology in the Medical School of St. Thomas's Hospital, London, and T. G. HILL, A.R.C.S., F.L.S., Reader in Vegetable Physiology in the University of London, University College. With diagrams. London, New York, Bombay and Calcutta: Longmans, Green & Co. 1913. pp. xii + 401. Price, $2.25.

The title of this book is possibly not the most appropriate one which could have been devised. The reviewer, at any rate, was surprised to find that the volume dealt with the chemistry of plants from a physiological rather than from a technological standpoint. The authors announce that their work was written in order to provide students of plant physiology with an account of the chemistry and significance in metabolism of the more important compounds found in plants. They have filled a real want, for no other work in English, good or bad, even approximately covers the same ground. Their treatment of the subject is in no sense encyclopedic, since it is intended rather to orient the student in a difficult field than to take the place of a work of reference such as Czapek's "Biochemie der Pflanzen." Only those compounds are treated which are of general occurrence or of special physiological importance in plants. A knowledge of elementary chemistry on the part of the reader is presupposed—otherwise the essentials of the subject could not have been brought within the convenient compass of 400 pages.

Notwithstanding the fact that most of the problems of plant physiology have to be attacked by chemical methods, there is not a university in this country where a good course in plant physiology is supplemented by adequate training in plant chemistry. Nevertheless, there is a continued demand for men to fill positions which require combined chemical and botanical training. To many students, therefore, Haas and Hill's book may be cordially recommended as a substitute for college courses which do not exist. It may be hoped, moreover, that the chemical departments of some of our universities will be encouraged by the appearance of so excellent a text-book to provide a course in biochemistry which will interlock, on the one hand, with the courses in plant physiology and on the other with the courses in organic and physical chemistry.

From the standpoint of either student or teacher, the book leaves little to be desired. The nine chapters correspond in general to the main groups of compounds which occur in plants. Each chapter presents a classification of the compounds which it includes, treats the more important members in some detail, often giving the methods for their quantitative estimation, and points out their physiological significance. The numerous bibliographic footnotes are especially to be commended.

H. H. BARTLETT

ELEMENTS OF WATER BACTERIOLOGY, with Special Reference to Sanitary Water Analysis. By SAMUEL CATE PRESCOTT, Associate Professor of Microbiology in the Massachusetts Institute of Technology, and CHARLES EDWARD AMORY WINSLOW, Associate Professor of Biology, College of the City of New York, and Curator of Public Health, American Museum of Natural History, New York. Third Edition, Rewritten. New York: John Wiley & Sons, Inc. 1913. pp. xiv + 318. Price, $1.75.

Since the first edition of Prescott and Winslow's little book on water bacteriology the publications on this subject have become more and more important both in America and in Europe. The literature is now so extensive that it would seem well nigh impossible for any one book to present it properly and at the same time with reasonable brevity. In this third edition of their text-book, which is in reality the second edition rewritten, Prescott and Winslow have attempted this task and have, we believe, done it successfully. As a necessary consequence, this edition is much enlarged, comprising now some 300 pages divided into twelve chapters. One of these chapters is devoted to shell-fish examination, an important addition and one especially welcome at the present time when the question of sewage pollution of shell-fish is so important. The principal facts and conclusions of earlier editions are brought out in the new one with, however, more elaborate discussion than formerly. In the main, the earlier conclusions as to the value of careful bacteriological analysis of water from a sanitary standpoint are adhered to and the authors still believe, as do the majority of American bacteriologists, that the isolation of intestinal bacteria from small quantities of water is the most valuable sign we have of sewage pollution. They also maintain their former position as to the superiority of bacterial counts of water made on gelatin at room temperature over those made on agar at the body temperature, but are inclined to admit that the latter procedure gives more valuable information than was originally supposed. In one important particular this edition differs from the earlier ones inasmuch as the authors have here adopted a new definition for the colon group of organisms. According to them "the colon group may be defined as including all aerobic non-spore-forming bacilli which produce acid and gas in dextrose and lactose media." In thus broadly defining this group of bacteria, Prescott and Winslow have departed from classical procedures and dogmas and it will be very interesting to see whether bacteriologists in America will follow them in their position. In this connection it should be pointed out that water has heretofore been condemned from a sanitary standpoint on the basis of finding in it a specific microorganism which is the predominant species in the human dejecta, namely, *Bacillus coli* of Escherich. Bacteriologists are in the main agreed about the cultural reactions of this species which were clearly and definitely given by the investigator who first carefully studied it and gave it its accepted name, although it must be admitted that the original description of this species has not been rigidly adhered to by subsequent workers. The isolation of this organism from water is of great value and, indeed, is the most delicate test we have at the present time for sewage pollution. As now defined by Prescott and Winslow, the colon group will comprise not only all organisms with the reactions of *Bacillus coli* but a variety of bacteria which differ from it in certain cultural features which have always been regarded as of specific value in the classification of bacteria. Such organisms were described years ago by Eisenberg, for instance, and named by him *Bacillus liquefaciens*, and attention has been directed to them by a number of observers abroad and in this country. They are not the *Bacillus coli* of Escherich. Such organisms might be included in the colon group on a broad basis but they have been isolated from the human dejecta only on rare occasions and while their presence in water may indicate sewage pollution, the point is not yet proved with such a degree of certainty as to justify the condemnation of water on this basis alone. There are in addition certain organisms widely distributed in nature in decaying vegetation, for instance, as the various species of the proteus group (*Bacillus proteus vulgaris* of Hauser) which produce acid and gas in dextrose and lactose media. The isolation of such organisms from spring water could hardly have a sanitary significance and yet they would be included in the colon group according to this definition. We are inclined to believe with the present evidence that the adoption of this broad definition of the colon group as given by Prescott and Winslow is likely to rob the colon test of some of its value without any corresponding benefit. Future experience will determine this point. In other respects this last edition represents a great improvement over earlier editions and can be most highly recommended to all students of Hygiene and Sanitation.

W. W. FORD

THE EXAMINATION OF WATERS AND WATER SUPPLIES. By JOHN C. THRESH, D.Sc., M.D. (VIC.), D.P.H. (CAMBR.). Second Edition, with 53 Illustrations. Philadelphia: P. Blakiston's Son & Co. 1913. pp. xx + 664. Price, $5.00.

The present edition of this standard work has been entirely revised and enlarged and several new chapters added. The book is divided into three parts: The first discusses the examination of sources of supply, something too often neglected by water analysts, and points out the possibilities of contamination corresponding to the various sources. The description of the uses of dyes, other chemicals and bacteria in detecting polluting sources is particularly interesting. Dr. Thresh's wide experience has given him an abundance of material for illustrations.

The second part deals with the interpretation of results of the chemical, microscopical and bacteriological examinations. In general, the interpretations and figures given will apply to waters in this country—the chlorine values being exceptions, as we rarely find good waters of such high chlorine content as recorded for England. Figures are given to show that smaller amounts of sewage pollution may be detected by bacteriological methods than by chemical, although the importance of the former method is somewhat lessened by the fact that empirical standards are often misleading. The author classifies waters from the bacteriological standpoint, on the basis of the presence or absence of *B. coli* in 100 cc. and spores of *B. enteriditis sporogenes* in 250 cc.

The third part gives the methods of analysis—chemical, microscopical and bacteriological—which are in use in his laboratory. These vary somewhat from the methods in use in this country. On account of recent discussions it is interesting to note that Dr. Thresh makes bacterial counts both at

20° C. and at 37° C. Records of a large number of analyses and some 36 plates illustrating the microscopical analysis of water are given.

The appendix contains methods of preparing solutions and a number of useful tables.

The book is the most complete work published on the subject, and this revision is a welcome addition to the literature of water analysis. JOHN F. NORTON

TRAITÉ DE CHIMIE MINÉRALE. . Par H. ERDMANN. Directeur de l' Institut de Chimie Minérale de la Technische Hochschule de Berlin. Ouvrage traduit sur la 5e edition allemande par A. CORVISY, Professeur Agrégé des Sciences Physiques au Lycée Gay-Lussac, Professeur Suppléant à l'École de Médecine et de Pharmacie de Limoges. Tome second: Étude des Métaux. Avec 76 figures et trois planches spectrales en couleurs. Paris: Librairie Scientifique A. Hermann et Fils. 1914. pp. 331. Price, Fr. 10.00.

The present book is the second and concluding volume of Corvisy's excellent translation of Erdmann's "Lehrbuch der anorganischen Chemie," the appearance of the first volume of which has already been noted in THIS JOURNAL.[1]

LES PROGRÈS DE LA CHIMIE IN 1912. Traduction française autorisée des "Annual Reports on the Progress of Chemistry for 1912, Vol. IX, issued by THE CHEMICAL SOCIETY, LONDON," et publiée sur l'initiative du Service de Recherches du Laboratoire Municipal de Paris. Traducteurs: MM. D. FLORENTIN, Chimiste au Laboratoire Municipal; E. GELIN, Chimiste contrôleur au Laboratoire Municipal; P. HUCHET, Licencié ès-Sciences, Préparateur au Laboratoire Municipal; M. DRECQ, Chef des Travaux de Physique à l'École de Physique et de Chimie de Paris; J. SAPHORES, Chef des Travaux de Physique à l'École de Physique et de Chimie de Paris; P. POURQUERY, Ingénieur-Chimiste, I. C. A. Paris: Librairie Scientifique A. Hermann et Fils. 1913. pp. xiv. + 411. Price, Fr. 7.50.

In the preface to this translation, Dr. André Kling, director of the Paris Municipal Laboratory, points out the need, in these days, of ever increasing complexity in the science of chemistry and the consequent necessity of narrower and narrower specialization by the individual worker, of some book that will bring before the chemist the gist of the more important work being done in other than his own special field. He then goes on to say: "In France, except for the Reviews of Chemistry, to which certain journals annually devote some pages, we have no such publication. And we cannot help being surprised at this lack when we consider that the French spirit is especially adapted to the realization of works of this kind, the object of which is to present in clear and concise form ideas confusedly buried in the prolixity of certain original memoirs.

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[1] Vol. **50**, p. 132.

. . . . The reason for this lack is of purely commercial origin, and if I have been compelled, for the present, to give up the idea of publishing, with the collaboration of specialists chosen from the various branches of chemistry, an Annual Review of the facts and ideas in chemistry, it has not been because I have been unable to find the men with the necessary ability and good-will, but simply on account of the hesitation of publishers, troubled by the crisis through which the French scientific book has passed." Being unable to bring out an original publication, Dr. Kling decided to offer his fellow-chemists speaking the French language a translation of a foreign book and his choice at once fell on the Annual Reports of the London Chemical Society. If the present volume meets with an encouraging reception, these Reports will be translated annually. C. A. R.

NEUERE ANSCHAUUNGEN AUF DEM GEBIETE DER ANORGANISCHEN CHEMIE. Von PROF. DR. A. WERNER in Zürich. Dritte durchgesehene und vermehrte Auflage. Die Wissenschaft. Sammlung von Einzeldarstellungen aus den Gebieten der Naturwissenschaft und der Technik. Band 8. Braunschweig: Druck und Verlag von Friedr. Vieweg und Sohn. 1913. pp. 419. Price, M. 12.00.

The "Neuere Anschauungen" of Werner is so well known that it would be superfluous to do more here than call attention to the appearance of the third enlarged edition. H. C. J.

INTRODUCTION à LA CHIMIE DES COMPLEXES. Théorie et systématique de la chimie des complexes minéraux. Par G. URBAIN et A. SÉNÉCHAL. Paris: Librairie Scientifique A. Hermann et Fils. 1913. pp. 477. Price, Fr. 15.

We read in the preface that "every chemical compound, whose formula contains a large number of atoms, should be called a complex. If we therefore except the elements and binary compounds of these with one another, the study of complexes is coextensive with that of chemistry itself."

One other section of the preface calls for special comment. The authors call attention to the tendency to-day of making everything practical. The results of an investigation are frequently regarded as of value just in proportion to the possibility of applying them to some useful end. The authors express their own minds on this point without any ambiguity. "We do not believe that the chemist can subscribe to this point of view. Science can and ought to exist independently of all industrial questions. It would be an era of decadence if all effort were considered sterile, and all investigations in vain, which did not have an immediate practical end." "We have on this point a profound conviction. The best service which the man of science can render to the engineer is to coordinate the science from which the engineer is to obtain profit, is to perfect the methods of reasoning and to establish the relations between cause and effect." This is really refreshing at a time when the "idealism" of the past seems on the wane, especially in those very quarters where we should least expect it to decay. The laboratory of the true man of science must be kept 180 degrees from the patent office in the future, as in the past, if science is to accomplish its highest good for mankind.

The book is divided into four parts of several chapters each. These are: Part I, Generalities; Part II, Perfect Electrolytic Complexes; Part III, Imperfect Complexes; and Part IV, Double Salts.

Any book on the subject of general inorganic chemistry from the pen of Urbain is welcome, because it comes from a leading investigator in this field—from a real master. H. C. J.

NOTIONS FONDAMENTALES DE CHIMIE ORGANIQUE. Par CHARLES MOUREU, Membre de Institut et de l'Académie de Médecine, Professeur à l'École supérieure de Pharmacie de l'Université de Paris. Quatrième édition, revue et mise au courant des derniers travaux. Paris: Gauthier-Villars. 1913.

The author has combined in this book both a text and a résumé of the recent progress in organic chemistry. The details concerning boiling points, specific gravities, etc., are omitted to a large extent, and the broader aspects of methods of preparation and interrelation of classes are given more attention. Such newer chapters as the Grignard methods, the reductions in alcohols in the sunlight discovered by Ciamician and Silber, etc., are given much more fully than usual. The book has much of interest and importance not ordinarily seen in texts. S. F. A.

ANLEITUNG ZUR DARSTELLUNG PHYTOCHEMISCHER UEBUNGSPRÄPARATE für Pharmazeuten, Chemiker, Technologen u. a. Von DR. D. H. WESTER. Mit 59 Textfiguren. Berlin: Verlag von Julius Springer. 1913. pp. xi + 129. Price, M. 3.60; bound, M. 4.20.

The excellent little book has, first, a very complete section on the technique required of pharmacists and chemists, the description of the apparatus being especially good. In the second part is given a list of preparations, including sugars, terpenes, tannins, alkaloids, enzymes, proteids, glucosides, waxes, fats, acids and alcohols. While the directions for the preparations are very good, the reactions are not discussed as fully as desirable. S. F. A.

TABLES ANNUELLES DE CONSTANTES ET DONNÉES NUMÉRIQUES DE CHIMIE, DE PHYSIQUE ET DE TECHNOLOGIE. Publiées sous le patronage de l'Association Internationale des Académies par le Comité International nommé par le VIIe Congrès de Chimie appliquée (Londres, 2 juin, 1909). Volume II, Année 1911. Paris: Gauthier-Villars; Leipzig: Akademische Verlagsgesellschaft m. b. H: London: J. & A. Churchill; Chicago: University of Chicago Press. 1913. pp. xl + 759.

This volume of physical constants should be accessible to every chemist interested in the quantitative aspect of chemical science. The accumulation of data is progressing so rapidly that it is practically impossible to read even the important articles, and difficult to remember just where to find certain facts desired. This book gives all the important data of 1911, in about 50 subjects, such as reaction velocities, conductivities, colloids, engineering, magnetism, essential oils, animal physiology, and organic chemistry. A personal letter from Mons. Marie to the reviewer indicates that more aid should be given the International Committee in order to allow the succeeding volumes to appear more promptly. S. F. A.

SMOKE. A Study of Town Air. By JULIUS B. COHEN, Ph.D., B.Sc., F.R.S., Professor of Organic Chemistry in the University of Leeds, and ARTHUR G. RUSTON, B.A., B.Sc., Science Tutor in the Department of Agriculture, University of Leeds. Illustrated. New York: Longmans, Green and Co.; London: Edward Arnold. pp. 88. Price, $1.40.

This small volume contains a considerable amount of very valuable material which the authors have obtained as a result of their own investigations of certain of the evils which result from the incomplete combustion of soft coal. These results are presented in a very clear style and the illustrations are excellent. Some very valuable material is presented on the effects of soot and sulphuric acid contained in smoke-polluted atmospheres upon the growth of vegetation and the corrosion of masonry and metal work. There is also included an appendix by Dr. Ascher on "The Influence of Coal-Smoke upon the Health."

The authors have confined their work to the study of the nature and quantity of soot in the air and the injurious effects of soot and sulphuric acid, without taking up the causes which produce smoke or methods for its abatement. Neither have the authors presented any data of their own upon the loss of heat which results from the incomplete combustion of coal of which smoke is an indication.

The book should be of considerable value to those interested in the question of smoke and its injurious effects. J. C. W. F.

HANDBUCH DER ARBEITSMETHODEN IN DER ANORGANISCHEN CHEMIE. Herausgegeben von DR. ARTHUR STÄHLER, Privatdozent an der Universität Berlin. Erster Band. Mit zahlreichen Abbildungen und Tabellen. Leipzig: Verlag von Veit & Co. 1913. S. xii + 742. Preis, M. 25.00; geb., M. 28.00.

This is the first of five volumes which are to constitute the completed *Handbuch* of the above title. It will be seen at once that the work is to be an extensive treatise, as the first volume contains 786 pages and is very profusely illustrated, which adds very much to its value.

It is not possible to attempt to review such a work as this with only one volume at hand, but the names of the fifty-eight well-known authors who are writing this *Handbuch* assure the value of the work when completed. It will be specially valuable as there is no work of recent date which treats this broad subject at all thoroughly, and the subject treated renders it equally useful to scientific and industrial laboratories.

The general arrangement of the five volumes is as follows: *Allgemeiner Teil*, Band I. Das anorganisch-chemische Laboratorium und seine Ausstaltung—Mechanische Operationen. Band II. Physikalische und chemische Operationen und Hilfsoperationen. Band III. Physikochemische Bestimmungen. *Spezieller Teil.* Band IV. A. Körperklassen. B. Elementen und Verbindungen der Gruppen 1–3. Band V. Elemente und Verbindungen der Gruppen 4–8—Register.

A brief outline of the contents of Vol. 1 is as follows:

The inorganic chemical laboratory and its equipment. The structural arrangement of the inorganic chemical laboratory (Alfred Stock). Objects for the equipment of the laboratory (Stähler, Groschuff, J. Bronn). Electrical equipment (Günther Schulze, Stähler). Heating and cooling arrangements (E. Schirm, Stähler, J. v. Wartenberg, J. Bronn, L. Weiss). General precautions for laboratory work (Stähler). Mechanical operations (Stähler, T. W. Richards). Assembling of apparatus. General operations.

The publishers state that the whole work will be completed within two years from the time of announcement. J. C. W. F.

TRAITÉ COMPLET D'ANALYSE CHIMIQUE APPLIQUÉE AUX ESSAIS INDUSTRIELS. Par J. POST, Professeur honoraire a l'Université de Goettingue, et B. NEUMANN, Professeur à la Technische Hochschule de Darmstadt. Avec la collaboration de nombreux chimistes et spécialistes. Deuxiéme édition française entierement refondue. Traduite d'après la troisième édition allemande et augmentée de nombreuses additions par G. CHENU, ING. E. P. C., Licencié os sciences, et M. PELLET, ING. I. N. A., Licencié os sciences Tome troisième, second fascicule. Goudron de houille, Matières colorantes. Avec 8 figures hors le texte. Paris: Librairie scientifique A. Hermann et Fils. 1913. pp. 465–902. Price, Fr. 15.00.

The book is a good translation of the fourth part of the second volume of the third German edition of Post's "Chemisch-technische Analyse," or that section of this well-known handbook on methods of chemico-technical analysis in which Prof. G. Schultz has dealt with coal tar, the mineral pigments, the natural and synthetic dyestuffs, and the color lakes, and which was lately reviewed in THIS JOURNAL.[1] The "numerous additions" mentioned on the title page evidently have reference to the new matter introduced by Prof. Schultz rather than to any considerable additions to the text made by the French translators.

S. P. MULLIKEN

TECHNICAL GAS AND FUEL ANALYSIS. BY ALFRED H. WHITE, Professor of Chemical Engineering, University of Michigan. International Chemical Series: H. P. TALBOT, Ph.D., Consulting Editor. New York: McGraw-Hill Book Company, Inc. 1913. pp. x + 276. Price, $2.00.

The author states in his preface that he has aimed in this book to present the conclusions of certain official committees and government bureaus which he names, and to indicate where there has been marked dissent from them. The work is more than a compilation, however, since it includes much valuable material derived from the author's own wide experience in the field of gas and fuel testing. There are 12 chapters (173 pp.) devoted to gas, one chapter (8 pp.) to liquid fuels, and 4 chapters (65 pp.) to coal. In view of the relatively great industrial importance of coal and the widespread efforts to increase efficiency in its use, and also in view of the rapidly increasing use of liquid fuels in modern industry, it seems that the author has unduly subordinated these two subjects to that of gas in a work on general fuel analysis.

The book is well suited to the use of engineering students or technical chemists who do not require the highest attainable degree of accuracy. The one chapter given on exact gas analysis is incomplete and might better have been omitted in a work of this character. This chapter presents some inexact methods, such as the use of Hempel pipettes with make-and-break connections, and the explosion method for methane and hydrogen, while omitting any description of the Haldane or Burrell apparatus for minute quantities of carbon dioxide and methane or of apparatus for analysis at constant volume. For students' use the book is perhaps lacking in explanation of underlying scientific principles; the inadequate treatment in Chapter I of the subject of solubility of gases in water and the effect of this on the accuracy of gas analysis is an example of this tendency. Chapter V on earlier types of apparatus is of no value to any one but a student of the history of the subject.

There are excellent chapters on the heating value and the candle power of gas and on the heating value of coal. Full descriptions, well illustrated, are given of various types of calorimeters and photometers, with ample and most useful explanations of sources of error and their relative importance. Sampling of coal is given a separate chapter and is treated thoroughly and well—much better than is the sampling of gases. The modern trend toward the purchase of coal on specifications lends peculiar value to such a chapter.

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[1] Vol. 44, p. 563.

For technical use, many of the methods given are too long and cumbersome; for example, methods for the absorption of hydrogen by palladous chloride solution or by a solution of colloidal palladium with sodium picrate. Many of the methods given, furthermore, have not been verified by the author and their reliability is questionable. The ammoniacal nickel cyanide method, presented in detail, for the determination of benzene in illuminating gas is one of several instances deserving such criticism.

The work does not enter the field of mine gases, or of ventilation and air analysis. It merely touches the subject of natural gas.

Some inaccurate statements appear: e. g. (p. 22), that burettes do not usually need calibration for technical work; (p. 172) that natural gas contains small amounts of oxygen and unsaturated hydrocarbons; (p. 57) that among a number of the paraffin hydrocarbons present in a gas any two may be determined by calculation from the results of combustion; and (p. 203) that a white ash from coal indicates high melting point. Among the few typographical errors, a particularly startling one appears on page 232 in the statement "the gas which disappears is oxygen in the proportion of one molecule for each 4 grams of hydrogen." It is to be assumed that "gram-molecule" is here meant, instead of "molecule." Under the heading of ash in coal, an erroneous impression is given that all coal contains sulphur in the form of sulphates to an extent "varying from a few tenths up to 1 percent." The possibility of contamination of coal samples by abrasion of iron surfaces or of flint pebbles in grinding should have been mentioned.

It is unfortunate that probable inaccuracies, such as the reporting of the presence of hydrogen and carbon monoxide in natural gas in the table on page 173, should be quoted from other authorities and their acceptance by the reading public thus promoted.

A number of convenient tables are added in the appendix. The book will find its most useful application in classes of advanced students of fuel engineering. HORACE C. PORTER

Der kolloide Schwefel. Von Sven Odén. Nova Acta Reglae Societatis Scientiarum Upsaliensis. Ser. IV, Vol. 3, N. 4. Upsala: Akademische Buchhandlung A.-G. 1913. pp. 193.

This is an exhaustive monograph on the history and properties of colloidal sulphur in which the author includes the results of three years of his investigation of this substance. One of the most important points relating to the author's work contained in the monograph is the working out of a method of "fractional coagulation" which permitted the preparation of a colloidal solution containing particles of practically the same size. It was not until this was done that it was possible to make a satisfactory study of the substance. The monograph also contains a list of references to articles on colloidal sulphur which is an important addition. J. C. W. F.

IN CONCLUSION

As stated in the November number This Journal now ends its existence as a separate publication and, beginning in January, 1914, it will become a part of the *Journal of the American Chemical Society.* A few words concerning this change seem called for here. First, as to how the American Chemical Journal came to be established. In a notice referring to the death of Professor James D. Dana, which appeared in Vol. **17**, 470 (1895), the editor said: "Up to the year 1878 the present writer had sent his chemical articles to the *American Journal of Science and Arts,* and they had been kindly received. In the year named, however, a number of articles were sent in together and, in the course of a few days, they were returned with a long and extremely friendly letter from Professor Dana, in which he made it clear that he could not publish the articles without entirely changing the character of his journal; and, at the same time, he strongly urged the starting of a chemical journal. The letter led to correspondence which resulted in the foundation of This Journal, the first number of which appeared in April, 1879. The editor of the new journal was entirely inexperienced in the work that devolved upon him, and he owes much to the wise counsel and friendly coöperation of Professor Dana."

At first, six numbers a year were published and there were many times when there was difficulty in filling these. By 1889 the supply of material had increased to such an extent as to lead to an enlargement. After this for seven years eight numbers a year were issued. Beginning in 1896, ten numbers a year were issued; and, finally, beginning in 1899, the journal became a monthly publication, and even then it was found difficult at times to take care of all the material that was sent in.

In the meantime the American Chemical Society has grown to great importance and is amply prepared to provide for the publication of all articles on chemical subjects likely to be prepared in this country. It is certain that if such a society had been in existence in 1878 the AMERICAN CHEMICAL JOURNAL would not have been started. Taking everything into consideration it now seems best to the editor to place the control of his journal in the hands of the society. It is needless for him to say that after thirty-five years of editorial work he does not now withdraw from it without a feeling of deep regret. His earnest hope is that the step may prove wise.

In this connection he wishes to give special thanks to his colaborer, Dr. Charles A. Rouiller, Assistant Editor, who for several years past has borne the principal burden of the work of editing.

I. R.

GENERAL INDEX TO VOLUMES XXI–L

A general index to Volumes 21–50, inclusive, of the AMERICAN CHEMICAL JOURNAL, will be issued early in 1914. Orders should be addressed to the Johns Hopkins Press, Baltimore, Md. Price, $1.50.

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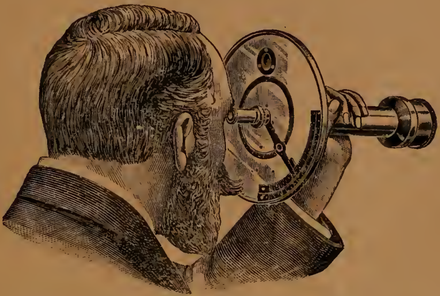

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